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PHYSICAL REVIEW.

SPECTROPHOTOMETRY OF NORMAL AND COLOR-BLIND EYES.

By F. L. Tufts.

I. Definitions of the Term "Equal Luminosity" as Applied to Colored Lights.

THE experimental determination of the relative luminosity of the different parts of a spectrum offers very serious difficulties, and, while a number of different types of instruments have been constructed for the purpose of making such measurements, most have shown defects either in the accuracy of the results obtained or in the matter of manipulation. Instruments of the type of the Vierordt double-slit spectrophotometer, or of the Brace spectrophotometer, are of course not of this kind, and while very convenient and accurate for the comparison of the relative luminosity of different sources of light in any given part of the spectrum, give no means of determining the relative luminosity of a given source in the different parts of its spectrum. All instruments for this latter purpose may be conveniently classified under three general types depending upon the definition of the term "equal luminosity," employed for the interpretation of the results obtained when comparing different colored lights. The three definitions most frequently employed are the following :

I. Two similar surfaces, illuminated respectively by two lights of different color, may be said to be of equal luminosity if, in the judgment of the observer, they appear equally luminous.

This definition presupposes in the observer the ability to form a

judgment concerning equality of luminosity, which is not influenced by differences in color. Concerning such judgments, Helmholz has remarked :[1]

"I must explain that personally, I put no confidence in my judgment concerning the equality in luminosity of differently colored surfaces. I admit, however, that of two differently colored fields, one can be so much darkened that there remains no doubt that the other is brighter."

Abney and Festing have constructed and used a spectro-photometer depending, in its action, upon this definition of the term "equal luminosity." By varying the luminosity of one of the surfaces until it appears first more luminous and then less luminous than the other, and taking a mean, they have been able to employ it in some very interesting photometric work.[2]

II. Two similar surfaces, white, with black markings on them, illuminated respectively by two lights of different color, may be said to be of equal luminosity if, when placed at the same distance from the eye, the details can be distinguished with the same minuteness.

According to this definition, the measure of luminosity is the amount of light, independent of color, which is necessary to enable one clearly to distinguish objects. A method of color photometry depending upon this definition of luminosity was very carefully developed by Maci de Lepinay and Nicati,[3] and they showed that the second definition is not always equivalent to the first. This method has been applied to the determination of the relation between energy and luminosity in different parts of the spectrum by Langley,[4] A. König,[5] and Pflüger.[6] A spectrophotometer has been constructed upon this principle by E. S. Ferry,[7] and used to determine the distribution of luminosity, according to this definition of it, in the light of a 16 candle-power Edison incandescent lamp. He also investigated the relation between luminosity as thus determined and persistence of retinal impressions in different parts of the spectrum.

[1] Handbuch der Physiologischen Optik, second edition, p. 440.
[2] Color Photometry, Trans. Roy. Soc. Lond., 1886, p. 423, and 1888, p. 547.
[3] Annales de Chimie et de Physique, 5th series, vol. 24, p. 30.
[4] Am. Jour. Sci., 36, pp. 359–380, 1888.
[5] Z. Psy. Phys. d. Sinnesorgane, 4, pp. 241–348, 1893.
[6] Ann. d. Physik, 9, pp. 185–208, 1902.
[7] Am. Jour. Sci., 44, pp. 192–207, 1892.

III. Two similar surfaces, illuminated respectively by two lights of different color, are said to be of the same luminosity if, on rapidly replacing one by the other before the eye, there is no sensation of flickering. Methods of color photometry depending upon this definition of equal luminosity have been developed by Rood,[1] Whitman[2] and Tufts.[3]

It has been shown experimentally that the luminosity, as thus defined, of a white or gray light formed by combining two or more colored lights, is equal to the sum of the luminosities of the colored lights so combined. The writer is not aware that the second definition has been subjected to such an experimental test.

A new form of spectrophotometer for the measurement of color luminosities according to definition III., is described in the present paper, and the results are given of measurements of the luminosities of the different parts of the spectrum as they appear to normal and to color-blind eyes.

II. Description of the Flicker Spectrophotometer.

The instrument consists of a spectroscope, Fig. 1, in which the telescope T and the axis of the rotating sectored disc D are rigidly

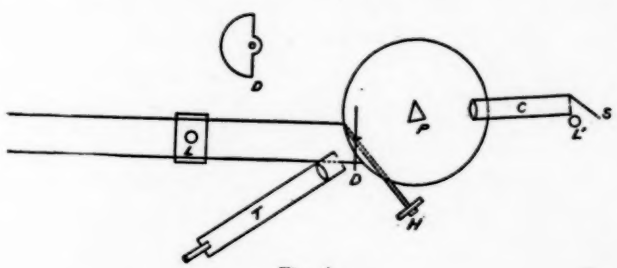

Fig. 1.

fastened to a table, while the colimator C, the prism P, the lamp L' and the white screen S are rigidly connected with the graduated circle of the spectroscope. This circle, together with the connected parts, can be rotated about a vertical axis through its center by means of a screw with a graduated head H. The light L is

[1] Am. Jour. Sci., September, 1893, September, 1899, October, 1899.
[2] Physical Review, vol. 3, no. 4, 1896.
[3] Trans. N. Y. Acad. Sci., XVI., April, 1897.

mounted on a photometer bar so that its distance from the white rotating disc D can be varied, and thus vary the luminosity of the disc. The disc D and the screen S are covered with white paper cut from the same piece. The eye-piece of the telescope is provided with a slot of adjustable width. Finally, the instrument is provided with black screens and diaphragms so placed that the photometric measurements can be made in a lighted room.

The adjustment and operation of the instrument are as follows: The lamp L' and the screen S, having been replaced by a Bunsen burner, the flame of which is colored with suitable salts, the spectroscope can be adjusted for minimum deviation of the sodium lines, and the screw H calibrated in terms of the wave-lengths of the light used. The lamp and screen may then be replaced, and the motor which rotates the disc D started. Through half of the revolution of this disc, the slit in the eye-piece is illuminated by the light from the lamp L which is reflected from the disc, while through the remaining half of the revolution it receives light of a given wave-length from the spectrum of the lamp L' reflected from the screen S through the colimator and prism. The speed of the motor rotating the disc D should be adjusted so as to give the best conditions for flickering in case there is any difference in the luminosities of the two lights. The distance of the lamp L from the disc can be varied until all flickering disappears, and the distance measured. By means of the screw H, any part of the spectrum can be made to illuminate the eye-piece slit, and its luminosity measured in terms of the luminosity of the white disc. The relation between the wave-length of any particular color and its luminosity (definition III.), in terms of the observer's white, can be plotted, using wave-lengths as abscissa, and luminosities as ordinates. The curve thus obtained will be referred to as the *wave-length luminosity curve* for the particular observer with the lights used.

Other means of adapting the flicker principle to a spectrophotometer were tried, but none proved so satisfactory as this, particularly for the testing of untrained observers. The writer has found that any person at all accustomed to looking through optical instruments, such as microscopes or telescopes, can obtain very uniform readings with this form of spectrophotometer, without any preliminary

training. By using a method of recording the distances of the lamp L from the disc, on a fillet of paper, described by Professor Rood,[1] the average observer can take ten readings for each of eight or ten positions in the spectrum, in from 20 to 25 minutes, and without any fatigue more than would be experienced in using a microscope or telescope for the same length of time.

III. Photometric Measurements with the Writer's Eyes.

The spectrophotometer just described was employed to investigate the relation between the luminosity of a white and the sum of

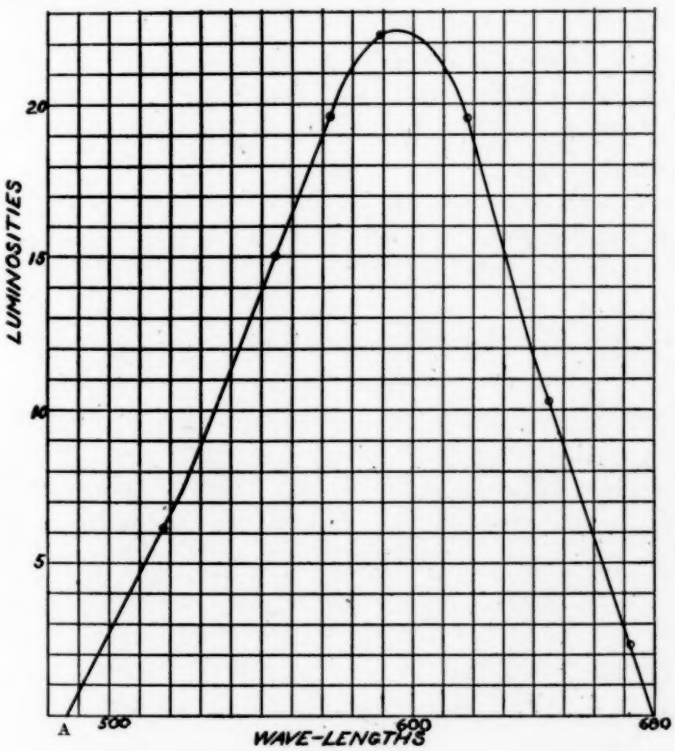

Fig. 2.

the luminosities of its constituent spectrum colors, according to definition III. of the luminosity of a colored light. The writer's wave-length luminosity curve for the reflected light from the lamp L' was determined. Each of the points recorded in Fig. 2 is the mean

[1] Amer. Jour. Sci., September, 1899.

of from ten to twenty readings. The prism P, Fig. 1, was then removed, and the colimator, together with the attached screen S and lamp L', turned into such a position that the image of the colimator-slit coincided with the slit in the eye-piece. The luminosity of the white slit was then measured in terms of the same white as was used in the measurement of the luminosities of the spectrum colors. The width of the image of the colimator-slit was measured in terms of the revolution of the micrometer-screw H, the extent of the spectrum between the positions A and B, Fig. 2, having been previously determined in terms of the same unit.

Following are the results of the measurements made:

Luminosity of the image of the white colimator-slit, in terms of the unit used in the wave-length luminosity curve, Fig. 2	395
Width of image of colimator-slit in revolutions of the screw H	0.15
Length of spectrum between A and B, Fig. 2, in revolutions of the screw H	4.80
Length of spectrum in terms of width of image of colimator-slit	32
Total spectrum luminosity $= \int_A^B$ lum. dl (where l is expressed in slit-widths) = area between the wave-length luminosity curve and the axis of abscissæ	408

One sees that the sum of the luminosities of the spectrum colors determined in this way is equal to the measured luminosity of the original white to within about 3 per cent., which is well within the error of spectrophotometric measurements. Other independent measurements gave similar results, the measured luminosity of the white being sometimes greater and sometimes less than the computed sum of the luminosities of its spectrum colors.

The above results are readily explained if we assume that there is, in the retina of the eye, a sense organ (we will call it the luminosity sense), which is affected in the same way by all visible radiation. The difference between the action of different wave-lengths upon this organ we will assume to be a difference in the magnitude, only, of the effect, and not in its quality.

Since in these experiments the luminosity of any color is measured in terms of the luminosity of the white of the particular observer, any change in the relative luminosity of the different spectrum colors as seen by this observer would not affect the relation of equality between the luminosity of the white of the observer and the sum of

the luminosities of its spectrum colors as seen by him. In other words, no matter how much one may change the quality of one's white, as, for example, by looking through colored glass, the luminosity of that white should always be equal to the sum of the luminosities of its spectrum colors if they also are seen through the same colored glass. Consequently, the area of the wave-length luminosity curve should be the same whether determined by using the naked eye or by making all of the observations through colored glasses, provided (and this must be carefully noted) that the distribution of luminous energy in the spectra of the two lights L and L' is the same.

With the lamps L and L' of different candle power, it is very difficult to obtain the same relative distribution of luminous energy in the two spectra. The lamps used by the writer were the ordinary 50 C.P. incandescent stereopticon lamps. These lamps were tested in the following manner: Two lamps, one at L and one at L' were adjusted for no flickering when the photometer was set in the red, the distance of the lamp L from the disc D being noted. The lamps were then interchanged and the adjustment repeated. The ratio of the luminosity of the red of one of the lamps to the luminosity of the same red of the other lamp was thus obtained. This ratio was also determined for the yellow-green and the blue of the spectrum. Unless the ratios were approximately the same, the lamps were rejected and others compared. After a number of such comparisons, two lamps were found for which the ratio did not differ in different parts of the spectrum by more than 8 per cent. of its mean value. These two lamps were used for the purpose of determining the wave-length luminosity curve for: I. The naked eye; II. The eye looking through a yellow glass; III. The eye looking through a red glass; IV. The same eye tooking through a very pale blue glass.

The four curves are plotted in Fig. 3. The crosses indicate the readings for the naked eye, the letters Y, R, and B, the readings for the same eye when looking through the colored glasses respectively. Measurements on the four curves showed them all to have approximately the same area.

When a deep cobalt blue glass was used which transmitted only

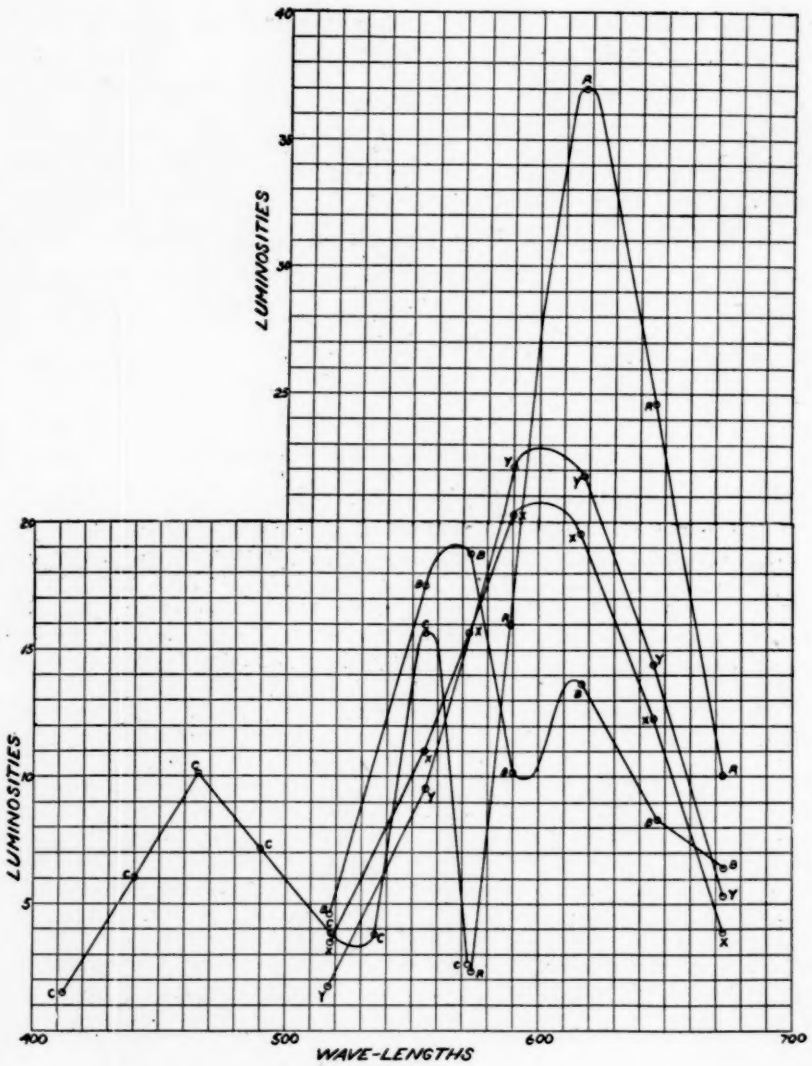

Fig. 3.

the extreme violet end of the spectrum, with a negligibly small amount of light in the red, the results were quite different. The wave-length luminosity curve for an eye looking through the cobalt glass is indicated in Fig. 3 by the letter *C*. If the area of this curve is compared with the area of the naked eye curve, it will be found to be almost 50 per cent. less. When the prism was removed

and the luminosity of the image of the colimator-slit determined by observations taken through the cobalt glass, the luminosity was found to be the same, within 2 per cent., as the luminosity determined by observations with the naked eye. It might seem, therefore, that for an eye looking through cobalt glass, the luminosity of the cobalt-eye's white was greater than the sum of the luminosities of its spectrum colors (def. 3). The phenomenon is possibly connected with the Purkinji effect and is still under investigation. The importance of this in the interpretation of the results obtained from observations with certain abnormal eyes is pointed out in the latter part of this paper.

The practical independence of our color and luminosity sensations is shown by the following experiments. It is well known that if one eye is exposed to a strong light through a green glass, for example, until the retina becomes fatigued, all objects appear to that eye as they would appear to the normal eye if it were looking through a red glass, transmitting a complementary color to the green. The color sense becomes fatigued by exposure to a given color, and it then reacts to stimuli in a way qualitatively different from the unfatigued sense. If our luminosity sense is independent of our color sense, and if its reaction is qualitatively the same for all wave-lengths within the visible spectrum, then it ought to be impossible to change the apparent luminosity of any color (measured in terms of the luminosity of the white of that eye) by fatiguing the luminosity sense of the eye with light of that particular color or its complementary. In other words, the wave-length luminosity curve for the fatigued eye should be identical with the wave-length luminosity curve of the unfatigued eye.

This assumption was tested experimentally in the following way: The wave-length luminosity curves were determined for the writer's two eyes, and were found to be practically identical. The right eye was then exposed to the light of a 100 C.P. incandescent lamp viewed through colored glass, the exposure being of sufficient duration to cause all white objects seen with the fatigued eye to appear of the complementary color to the light transmitted by the glass. The luminosity of a given spectrum color was then measured with the fatigued eye, and, immediately after, remeasured with the un-

fatigued eye. This was done for seven different positions in the spectrum. The right eye was refatigued just before each set of readings, and, in every case, the effect of the fatigue was of sufficient duration to give the complementary color effect after the set of readings had been taken.

The readings with the right eye fatigued by blue light were compared with the readings of the left, unfatigued eye, and the results

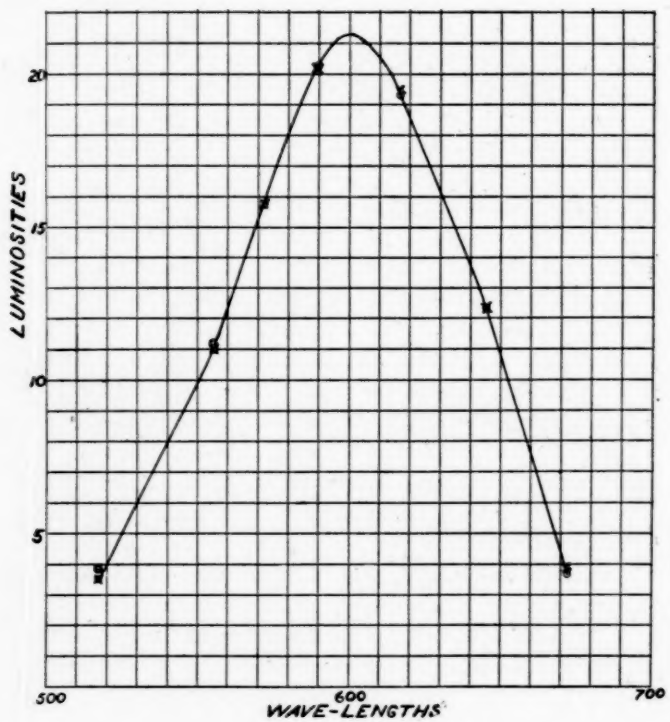

Fig. 4.

are given in Fig. 4. The crosses indicate the readings with the unfatigued eye, the circles, the readings with the fatigued eye. In every case the difference was found to be within the experimental error. Similar results were obtained by fatiguing the right eye with yellow and green lights. In every case the right eye was fatigued by looking at the incandescent filament through the colored glass, the eye being placed so near the filament that the area of the retina

covered by the image was many times the area covered by the image of the slit in the eye-piece of the spectrophotometer.

When a red glass was used (the same piece as was used for the red curve in Fig. 3) and the exposure only sufficient to produce the complementary color effect, the results obtained were similar to those obtained with the other colors. A continuous exposure, however, of several minutes, gave photometric readings with the fatigued eye which were very different from those with the normal eye. The

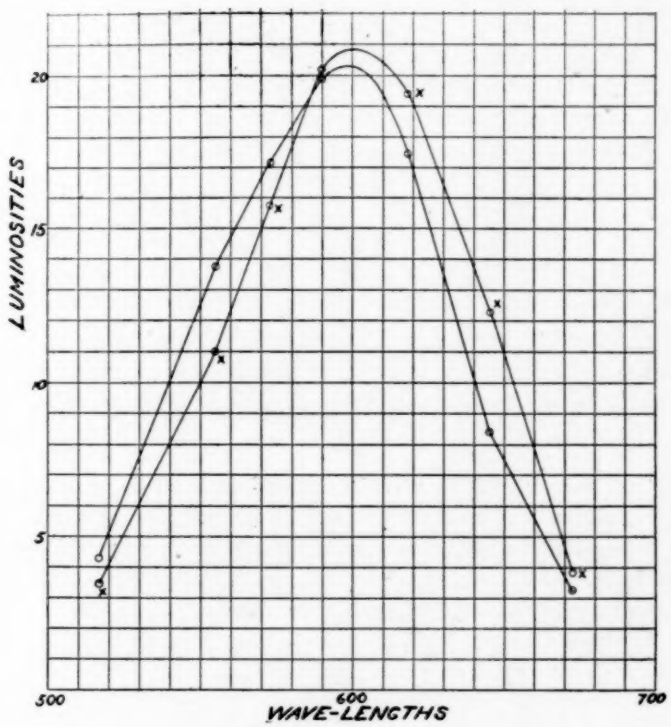

Fig. 5.

general character of the differences is shown in Fig. 5, the crosses indicating the curve for the normal eye, and the circles without crosses the readings for the fatigued eye. An inspection of the figure shows that the effect of a prolonged exposure of the retina to the long, or red rays, is to displace the maximum of the wave-length luminosity curve towards the blue end of the spectrum. This displacement is apparently due to some action of the long waves upon the lumi-

nosity sense, and is either not connected at all, or at least only indirectly, with their action upon the color sense, for the photometric readings became the same for the fatigued as for the unfatigued eye long before the vivid green after-image had disappeared.

The right eye was then fatigued by looking at the 100 C.P. lamp directly, so that vivid, colored after-images were seen as the eye recovered. The photometric readings were, however, the same for the fatigued as for the unfatigued eye. The fatigued eye was always focussed, in taking the readings, so that the image of the slit in the eye-piece was in the center of the after-image of the spiral lamp-filament. The photometric readings, however, did not change, although the background formed by the after-image changed its color as the eye recovered from its fatigue.

The above experiments show that the relative reaction of the luminosity-sense to white light and to light of different colors is not affected by ordinary fatigue produced by exposing the eye to colored or white light, but may be altered by prolonged exposure to red light. Two other persons possessing normal color vision have been kind enough to subject their eyes to the rather harsh treatment required by these experiments, and the results were, throughout, similar to those obtained from the writer's eyes. A change in the relative reaction of the luminosity sense to white and to colored lights was produced only by prolonged exposure to red light, exposure to yellow, green, blue, or white light, and moderate exposure to red, producing no similar effect.

IV. Comparison of the Wave-length Luminosity Curves of Different Eyes.

A number of different persons were kind enough to give the time required for the determination of their wave-length luminosity curves by the flicker spectrophotometer. Some twenty persons in all were examined, an effort being made to secure as many color-blind persons as possible, so that out of the twenty, six showed, by the ordinary Holmgren test, marked red-green blindness (the reds, greens, and grays, being confused in the sorting of colors). Of the fourteen persons possessing normal color-vision, according to the Holmgren test, ten showed a wave-length luminosity curve which

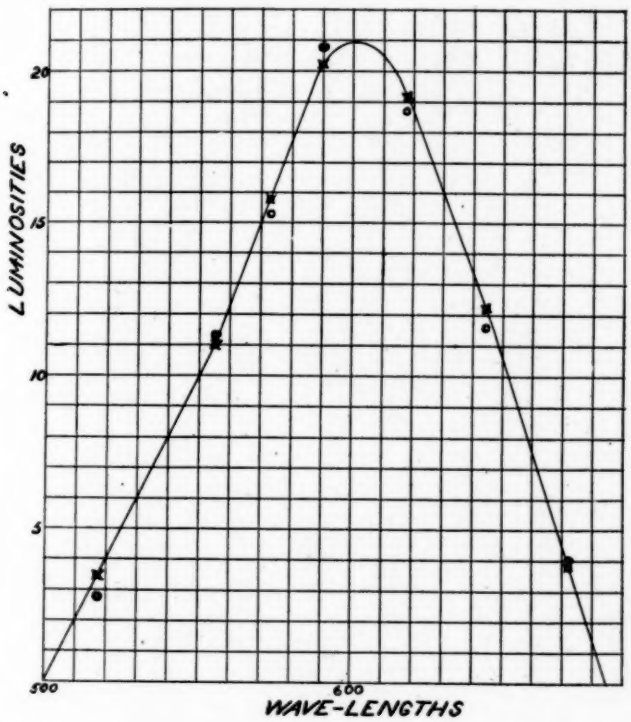

Fig. 6.

differed only slightly from the writer's curve. Representative readings for one of these observers are given in Fig. 6. The crosses indicate the writer's readings, and the circles the readings of one of the ten observers. The results, in both cases, are the mean of ten observations in each position in the spectrum.

Four of the persons studied showed a wave-length luminosity curve differing only slightly from the writer's, but the deviations were all in the same general direction, and seemed to indicate a rather distinct type of curve. One of these curves, which is representative of the four, is given in Fig. 7, and for comparison the writer's curve, indicated by crosses, is also given. The luminosity-sense of these persons seems to be less responsive to yellow, and correspondingly more sensitive to red and violet light, than the normal, thus giving a slightly flattened wave-length luminosity curve. All four persons seem to possess perfectly normal color vision.

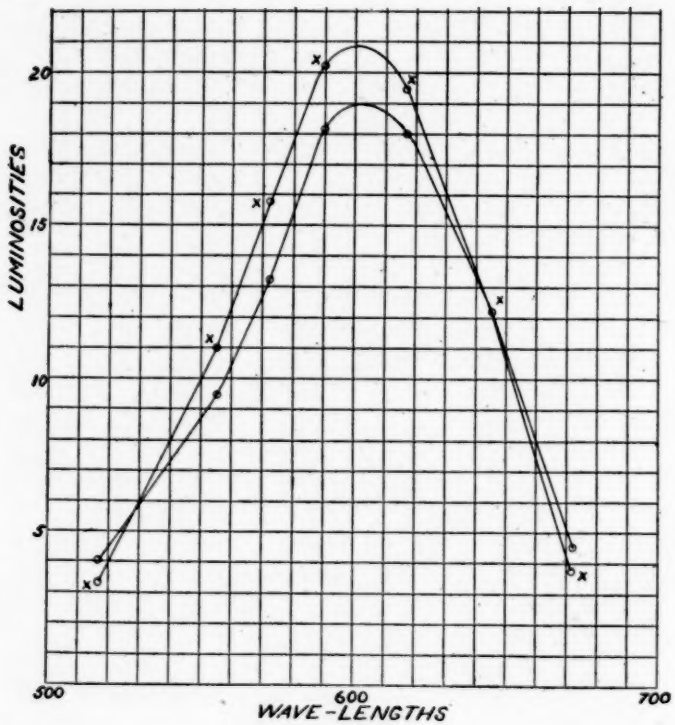

Fig. 7.

Two persons examined showed curves differing very much from the writer's. One of these, and it is almost identical with the other, is given in Fig. 8, the writer's curve being again indicated by the crosses. It is seen that the observer is more sensitive to red and less sensitive to green and blue than the writer. In other words, his wave-length luminosity curve is displaced toward the red end of the spectrum, with respect to the writer's curve. Neither of these persons made any mistake in sorting ordinary colors, but when asked to sort some extremely pale shades, both showed a slight tendency to confuse the oranges and yellow-greens.

Two other observers, both possessing perfectly normal color-vision as shown by the Holmgren test, with pronounced and also extremely pale shades of colors, gave wave-length luminosity curves that were displaced toward the green, with respect to the writer's curve. The curves also showed the peculiarity of having an area

distinctly less than that of the writer's curve. These two persons were kind enough to give the time necessary to repeat the complete set of readings on several different days; and the readings of each set were found to agree, within a few per cent., with the corresponding readings of any other set. The readings for the observer showing the greater deviation from the writer, are indicated in

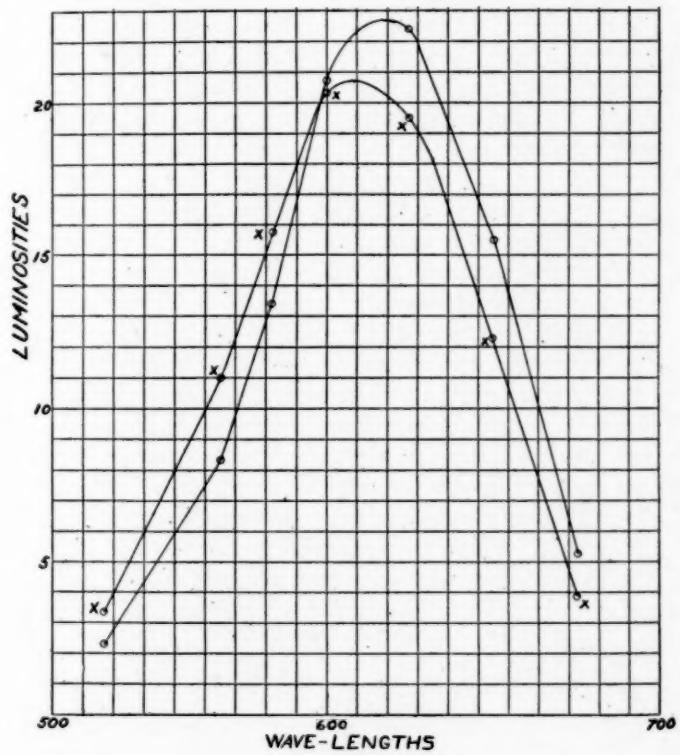

Fig. 8.

Fig. 9 by the circles, the writer's curve being indicated by the crosses. The position of maximum luminosity is seen to be displaced by a very considerable amount toward the green, and the area of the curve is less than the area of the writer's curve by as much as twenty per cent. The curve for the other observer is indicated by the dotted line in Fig. 9. The blue end of the spectrum must supply a much larger per cent. of the luminosity of the white of these observers than is the case with the normal eye, and

the smaller area of the curves might be expected after the observations with the cobalt glass described in part III. of this paper.

The observer whose curve differed most from the writer's curve, in Fig. 9, was also tested by the ordinary flicker photometer with

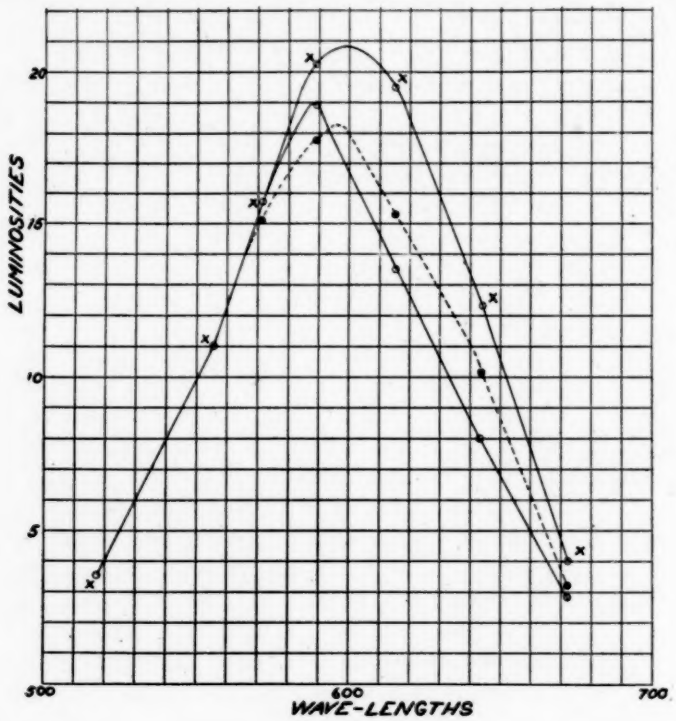

Fig. 9.

colored glasses, the method being the same as that employed by Professor Rood.[1] The results, expressed in terms of the same standard as that employed by Rood, are as follows, for the writer and the observer mentioned above:

Observer.	Apparent Luminosity of the Color.		
	Red.	Green.	Blue.
Rood's normal eye	100	100	100
Writer's eye	90	100	88
Observer's eye, Fig. 9	36	100	87

[1] On Color Vision and the Flicker Photometer, by Ogden N. Rood, Am. Jour. of Science, Vol. VIII., October, 1899.

It is therefore evident that an observer may be abnormally weak in the luminosity impression produced by a given color of light, and still be perfectly normal with respect to color sensations.

Six persons, all showing very marked red-green color-blindness by the Holmgren test, very kindly offered to give the time necessary for the determination of their wave-length luminosity curves. All

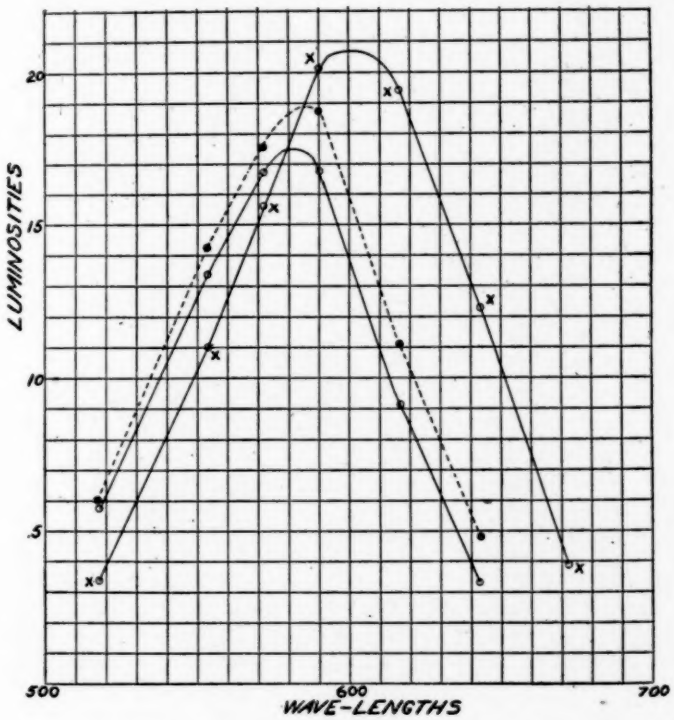

Fig. 10.

six persons confused the reds, greens, and grays, in the sorting of colors. Of the six persons, three were found to have wave-length luminosity curves in which the point of maximum luminosity was displaced towards the green, while the other three showed a displacement towards the red.

Of the first three curves, the one differing most and the one differing least from the writer's curve are given in Fig. 10, the writer's curve being indicated by crosses. All three of the curves had a much smaller area than that of the writer's curve, as might be expected after the experiments with the cobalt glass.

Of the second group of curves, showing a displacement of the maximum towards the red, the one differing most and the one differing least from the writer's, are given in Fig. 11. An inspection of these curves shows the areas to be nearly the same as the area of the writer's curve, and neither curve differs from the writer's

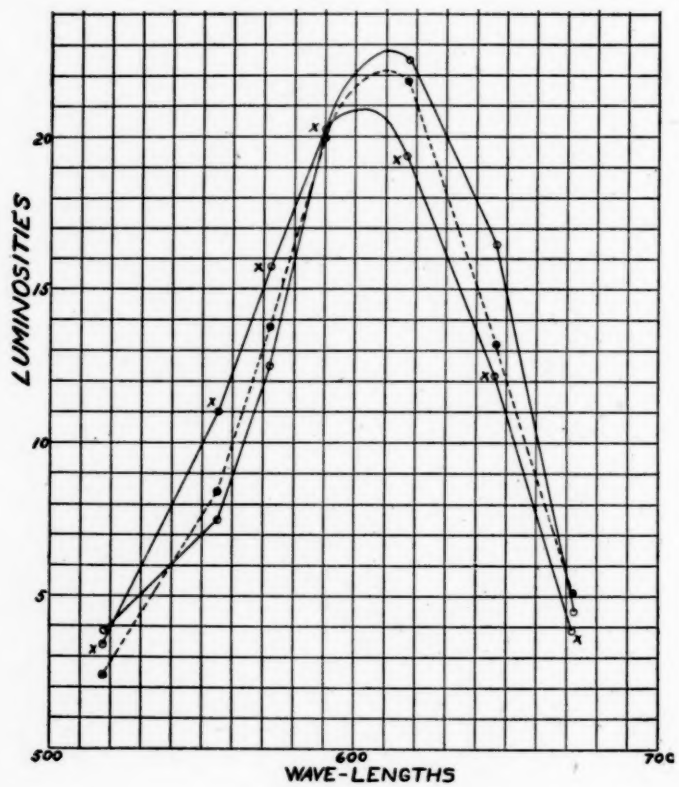

Fig. 11.

any more than the observer's curve in Fig. 8. Yet the observer of Fig. 8 showed no trace of color-blindness by the ordinary Holmgren test, while both of these observers were pronouncedly red-green color-blind.

While, therefore, the effect of light upon the color sense seems to be quite independent of its effect upon the luminosity sense, it would seem that an abnormal color sense is usually, if not always, associated with an abnormal wave-length luminosity curve. The

converse of this, however, is not true, and persons may be quite abnormal with respect to their color luminosity sense, and still be able to make pefectly normal judgments in sorting and matching colors.

It is well known that the peripheral portion of the retina is more sensitive to the luminous energy in the blue end of the spectrum than is the central portion (macula lutea), and the peripheral portion is known to contain a larger per cent. of rods than the central portion. If we assume that the wave-length luminosity curve for the rods is, with reference to the curve for the cones, displaced towards the blue end of the spectrum (and this seems the simplest explanation of these phenomena), then the differences in the positions of the maxima in the wave-length luminosity curves of different observers might be explained as due to differences in the ratio of rods to cones in the fovea centralis, if such a difference should be found to exist. Since it seems to be just as common for color-blind people to have wave-length luminosity curves displaced towards the red as towards the blue end of the spectrum, with reference to the normal curve, if the above explanation is accepted for the abnormal curves, it will not be possible to explain color-blindness as due to an abnormally large per cent. of rods in the fovea, as has sometimes been suggested (it being assumed that the cones alone contained the color sense organ).

While at present we have hardly sufficient data upon which to found a satisfactory theory of color vision, the above explanation of the differences in the luminosity of different colors (def. III.) as they appear to different observers seems to account very well for the phenomena described in this paper. Fatigue phenomena with color-blind eyes promise to give more definite information along these lines, and they are at present being investigated by the writer.

The form of flicker spectrophotometer here described lends itself readily to the determination of the per cent. of any spectrum color which must be mixed with a white of the same luminosity in order to be just discernible by the eye. Measurements which have been made upon normal eyes seem to give quite uniform results. Owing, however, to the difficulty of securing color-blind subjects who can give the requisite amount of time for the photometric tests, the collection of data is necessarily slow.

SUMMARY.

The results of the present investigation may be summed up as follows:

I. The retina of the human eye contains two distinct sense organs — one, the luminosity sense, the other, the color sense.

II. The luminosity sense is affected qualitatively in the same way by light stimuli of all wave-lengths within the visible spectrum so that it reacts, after fatigue, always in the same way, no matter what kind of light is used to fatigue the retina. (The only exception to this is when the fatigue is caused by prolonged exposure to the long, or red, rays of the spectrum.)

III. The relation between wave-length and luminosity (def. III.) in the case of a 50 C.P. incandescent lamp may be represented by a wave-length luminosity curve which, for most eyes, is identical with the curve in Fig. 6.

IV. Deviations from this normal curve fall, for the most part, into one or the other of two classes: (1) The point of maximum luminosity may be displaced towards the red, as in Fig. 8. (2) It may be displaced towards the green, as in Fig. 10.

V. Persons possessing perfectly normal color vision may have an abnormal wave-length luminosity curve, and color-blind persons as often have a wave-length luminosity curve belonging to class 1 as to class 2.

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June, 1907.

GENERAL LAW FOR VAPOR PRESSURES. PART II.

By Sanford A. Moss.

IN the preceding article[1] was deduced a general law connecting saturation temperatures and vapor pressures for all substances, on the basis of a relation given by Ramsay and Young. The law connects the absolute saturation temperatures T_a and T_b of two substances, corresponding to the same vapor pressure, by the symmetrical relation

$$\frac{1}{T_b} = c\frac{1}{T_a} + k \qquad (1)$$

c and k are constants for each pair of substances, for all vapor pressures. Either substance may be a vaporizing liquid or a subliming (volatilizing) solid. The two temperatures might also refer to the solid and liquid phases of the same substance.

Forms equivalent to (1) have also been derived from Ramsay and Young's relation by Ayrton and Perry[2] and J. D. Everett.[3]

As in the case of the original relation given by Ramsay and Young, we may determine by the law (1) the entire vapor pressure curve for a substance from two observations and the known curve of some standard substance.

In the preceding article the form (1) was supposed to be equivalent to the relation given by Ramsay and Young. However, it turns out that there are two quite different forms in which the statement of Ramsay and Young may be expressed mathematically. One form leads to the symmetrical law (1) and the other to a quite different non-symmetrical form. The latter form seems to be the one preferred by the authors of the original relation.

The purpose of this paper is to go into details in this matter, and

[1] Physical Review, Vol. 16, 1903, p. 356.
[2] Phil. Mag., Vol. 21 (series 5), 1886, p. 259.
[3] Phil. Mag., Vol. 4 (series 6), 1902, p. 335.

to show that the symmetrical law (1) is to be preferred over the other form for many reasons, and that it is very nearly, if not exactly, a law of nature. A number of related points discussed in various isolated papers will also be brought together systematically.

TEMPERATURE RATIO LAWS AND COMPARISON WITH OBSERVATIONS.

A relation exactly equivalent to (1) is

$$T_a/T_b = kT_a + c. \qquad (2)$$

Hence we have the following as a consequence of the symmetrical law (1). If values of T_a/T_b, the ratio of absolute saturation temperatures at same vapor pressure for two substances, be found for various vapor pressures, and plotted against T_a, the *numerator* of the ratio, the points will lie on a straight line.

The fact that saturation temperature observations satisfied a law similar to the one just stated, was the particular point originally brought out by Ramsay and Young. At times they used the identical law above given, and at times another form, as will be discussed presently.

In this work, Ramsay and Young found that the constant k was always small so that the term kT_a is comparatively small as compared with c. Hence T_a/T_b is nearly but not quite constant. For the case of pairs of substances from a homologous series, such as the various ethers, k is zero, and the ratio T_a/T_b is exactly constant.[1]

Now Ramsay and Young in some cases and Travers in all cases plot the absolute temperature ratio of (2) not against the *numerator*, but against the *denominator*. That is, they use the reciprocal of the left hand member of (2), corresponding to the dissimilar and non-symmetrical form

$$T_b/T_a = k'T_a + c'. \qquad (3)$$

Evidently, if values of T_a/T_b give a straight line when plotted against values of T_a, so that (2) is satisfied, then values of the reciprocal, T_b/T_a, will not give a straight line but a curve. It will probably always be very flat, however, but nevertheless such that (3) is

[1] Phil. Mag., Vol. 20, series 5, 1885, p. 530; Vol. 21, series 5, 1886, p. 33; Vol. 22, series 5, 1886, p. 37. Here the constant above called k is called c.

not exactly satisfied. If the values used are from observations and are slightly irregular, and if the range covered is not very great, the points may seem to follow a linear law, and may apparently satisfy the non-symmetrical form (3). It will be shown however that the points from various published observations fall in a straight line at least as well and often better, if the symmetrical form (2) is used rather than the non-symmetrical form (3) and also that it is more rational to use the symmetrical form.

In the original paper on the subject, by Ramsay and Young,[1] the law is given as being that the ratio of absolute saturation temperatures is a linear function of one of them. There is no statement as to which one, numerator or denominator. In the paper are given tables for the cases of ethyl alcohol, C_2H_6O, methyl alcohol, CH_4O, ethyl oxid, $C_4H_{10}O$, ethyl bromide, C_2H_5Br, ethyl chloride, C_2H_5Cl, ethylene, C_2H_4, oxygen, O_2 (3 comparisons), and mercury, Hg, obtained by plotting actual vapor pressure observations according to the symmetrical form (2). That is, saturation temperature ratios are plotted against numerators. The law is shown to be verified as the observations lie very nearly on a straight line.

On the contrary, the opposite and non-symmetrical form (3) is used for a number of other substances and temperature ratio is plotted against denominator. No note is made regarding the change in procedure. Aryton and Perry have made some remarks on this paper[2] and also seem to have noted the two different forms used. As already stated they deduce a form equivalent to (1) which they also regard as preferable on account of symmetry.

For the case of carbon bisulphid, CS_2, one of the substances for which Ramsay and Young use the non-symmetrical form, the writer has replotted the given figures in the symmetrical form. The resulting points lie equally well on a straight line. A similar situation doubtless exists with the other cases where the non-symmetrical form was used, and the symmetrical form would undoubtedly have given at least as good results.

The paper gives as an algebraic expression of the law

$$R' = R + k(T' - T).$$

[1] Phil. Mag., Vol. 21, series 5, 1886, p. 33.
[2] Phil. Mag., Vol. 21, series 5, 1886, p. 259.

(The constant k is called c in the paper.) R and R' are ratios of absolute saturation temperatures of two substances at same vapor pressure, for two different vapor pressures. T and T' are temperatures of one of the substances. No statement is made as to which one, that of the numerator or denominator of the ratios. It is readily seen that this expression is equivalent to (2) or to (3) according as one or the other is used.

A similar expression is given by Ramsay and Travers in the classic paper, "Argon and its Companions,"[1] and is repeated on page 236 of Travers' "Study of Gases." This is printed in both places.

$$\frac{T_a}{T_b} = \frac{T_a'}{T_b'} + k(T_a - T_a').$$

However, the writer has been informed by Professor Travers that this is a mistake and that the last parenthesis should have been $(T_b - T_b')$, as is also indicated by the context. This correction calls for plotting of temperature ratio against denominator, contrary to the symmetrical form (2). In the paper on argon, and in "Study of Gases," examples are given of the application of the law and temperature ratios are always plotted against denominator. This may therefore be considered as the form of law preferred by Ramsay and Travers.

The preceding paper was based on the statement of the law given immediately above and the symmetrical form (2) deduced therefrom. The fact that the formula was not printed as the authors intended was not known to the writer at the time. The whole of the preceding paper goes to show that the symmetrical form (2) is correct, regardless of the fact that it was deduced from a misprint; and additional evidence is given in this paper.

In the paper, "Argon and its Companions," observed values of vapor pressure of krypton, argon and xenon are given, agreeing fairly well with the form (3). The writer has replotted these observations, using instead the form (2), and has found much better agreement. For the case of krypton two observations are not included in the range of the chart given by Ramsay and Travers, and these do not

[1] Phil. Trans., Vol. 197 A, 1901, p. 68.

lie on an extension of the line through the other points. However, when reciprocals of the ratio are used, corresponding to the form (2), these points, as well as all of the others, fall almost exactly on a straight line. In the case of argon, the form (2) fits slightly better than the other form, while in the case of xenon there is no material difference, owing to observational irregularities. Ramsay and Travers give tables of vapor pressures of argon, krypton and xenon, smoothed by the use of the form (3). Evidently the use of (2), the form preferred by the writer, would give slightly different tables.

The form (2) has been applied by the writer to Miller's observations of vapor pressure of SO_2[1], and found to agree very well for moderate temperatures, but to give some discrepancy at high values, The relation between T_s, the saturation temperature of SO_2, and T_w, that of water vapor for the same pressure, is found to be

$$\frac{1}{T_s} = 1.6667 \frac{1}{T_w} - 0.00036.$$

In the preceding paper was given a table, reproduced herewith with some additions, for vapor pressures of water as computed from Ramsay and Young's observations on methyl alcohol by means of the law,

$$\frac{1}{T_w} = .9198 \frac{1}{T_a} - 0.0000307.$$

TABLE OF HIGH SATURATION TEMPERATURES OF WATER VAPOR.

Vapor Pressure. mm. Hg.	Saturation Temperatures, Degrees Centigrade.		
	From Methyl Alc. Obs.	From Cailletet's Obs.	From Formula "K."
45,000	275.9	274.8	276.0
50,000	282.9	281.5	283.0
55,000	289.3	288.0	289.5
60,000	295.2	294.0	295.6

Since the original table was published, observations by Cailletet have come to the attention of the writer, and interpolations from them are given in the table. They are very close to the computed figures, although slightly lower. It may be remarked however, that for lower pressures, Cailletet's temperature observations are slightly lower than those of both Regnault and Ramsay and Young,

[1] Trans. Amer. Soc. Mech. Engrs., Vol. 25, 1904, p. 182.

suggesting that all of his values may be slightly low. If so, the computed values are evidently almost exactly correct. The last column of the table will be referred to later.

INVESTIGATION OF RATIONALITY OF THE TEMPERATURE RATIO LAWS.

The law expressed by (1) is obviously mutual and $1/T_a$ and $1/T_b$ are each linear functions of the other. Similarly we may reverse (2) by writing it,

$$\frac{T_b}{T_a} = \left(-\frac{k}{c}\right) T_b + \frac{1}{c}.$$

Hence if we plot the reciprocal of the ratio on the left of (2) against the new numerator, we also have a linear relation. Hence if we use the form (2) it is immaterial as to which of a pair of substances is used as numerator or denominator. In other words the symmetrical form of the temperature ratio law is rational in so far that it is perfectly reversible.

The non-symmetrical form (3) does not turn out thus however. We may write it

$$\frac{T_a}{T_b} = \left(-\frac{k'}{c'}\right) \frac{T_a^2}{T_b} + \frac{1}{c'}.$$

Hence if T_b/T_a is a linear function of the denominator, T_a/T_b is not a linear function of the new denominator.

Hence if the form (3) is used for a given pair of substances, different results are obtained according to the one used as denominator and if the law holds in one form, the ratio cannot be inverted.

Another evidence of the rationality of the forms (1) and (2) is the fact that if the law holds for pairs consisting of two substances each compared with a third standard substance, it will necessarily hold for the pair consisting of the two different substances from the original pairs. Suppose for instance that the law holds for substances a and b and also for substances a and d. Then

$$\frac{1}{T_b} = c \frac{1}{T_a} + k,$$

$$\frac{1}{T_d} = c' \frac{1}{T_a} + k'.$$

All of the temperatures correspond to the same vapor pressure. By eliminating $1/T_a$ from the two equations we obtain

$$\frac{1}{T_b} = \left(\frac{c}{c'}\right)\frac{1}{T_d} + \left(k - k'\frac{c}{c'}\right).$$

Thus the linear relation holds for the pair of substances b and d.

On the contrary this does not occur with the form (3), and if two pairs of substances satisfy it, there is not satisfaction after interchange. Using the form (3) in the above case

$$\frac{T_a}{T_b} = kT_b + c.$$

$$\frac{T_a}{T_d} = k'T_d + c'.$$

Eliminating T_a by division,

$$\frac{T_d}{T_b} = \frac{kT_b + c}{k'T_d + c'}.$$

Hence the ratio T_d/T_b is not linear in the denominator T_b so that the law is not satisfied.

As already shown, the original relations of the case just investigated are not exactly reversible. Hence by using other arrangements of subscripts in them, we can obtain three more expressions for T_d/T_b all complicated and not giving the desired linear relation.

The point here discussed was originally mentioned by Findlay,[1] who showed it however by using relations only one of which was according to the non-symmetrical form (3), the other being according to the symmetrical form (2).

No doubt many sets of observed points would fit either of the forms fairly well on account of the flatness of the reciprocal curve for the short range usually covered, and the inevitable observational irregularities. However, the fact that the forms (1) or (2) permit of reversal and interchange makes them preferable if for no other reason.

Similar remarks apply to laws of the same form as (2) announced[2]

[1] Zeit. phys. Chemie, Vol. 42, 1902, p. 110.

[2] Roy. Soc. Proc., Vol. 69, 1902, p. 471.

by Findlay for both chemical solubilities and equilibrium constants as functions of absolute temperature, instead of vapor pressures.

LATENT HEAT RATIO LAWS.

By differentiating (1) with respect to p, we obtain an expression which forms the basis of further relations

$$\frac{T_a^2 \frac{dp}{dT_a}}{T_b^2 \frac{dp}{dT_b}} = c.$$

For future purposes we write this

$$c \frac{\frac{1}{T_a}\frac{dT_a}{dp}}{\frac{1}{T_b}\frac{dT_b}{dp}} = \frac{T_a}{T_b}. \tag{4}$$

We also use the well-known thermodynamic relation for saturated vapor

$$\frac{u}{r} = \frac{1}{AT}\frac{dT}{dp},$$

where A is reciprocal of mechanical equivalent of heat, r is latent heat of vaporization, and u is difference between specific volumes of vapor and liquid. Except near the critical point, u approximates to the specific volume corresponding to saturation pressure and temperature, given by the perfect gas law and the molecular weight. By substituting from the last relation in (4)

$$c \frac{u_a/r_a}{u_b/r_b} = \frac{T_a}{T_b}, \tag{5}$$

From (2) it follows that

$$\frac{\frac{1}{T_a}\frac{dT_a}{dp}}{\frac{1}{T_b}\frac{dT_b}{dp}} = 1 + \frac{k}{c} T_a, \tag{6}$$

$$\frac{u_a/r_a}{u_b/r_b} = 1 + \frac{k}{c} T_a, \tag{7}$$

$$\frac{Apu_a/r_a}{Apu_b/r_b} = 1 + \frac{k}{c} T_a. \tag{8}$$

In other words, the ratio of either of the quantities $1/T\,dT/dp$, Apu/r or u/r, for two substances at the same vapor pressure has the same property as the ratio of absolute saturation temperatures, and is a linear function of the absolute temperature corresponding to the numerator. We remark that Apu/r is the ratio of external to total latent heat of vaporization, and that u/r is increase of volume per unit addition of latent heat. These laws, as in the case of the primary law, apply to subliming solids as well as to vaporizing liquids.

As stated, Ramsay and Young have shown that the constant k, and hence also k/c, is always very small, and is zero for homologous substances. Hence the quantities referred to are nearly alike for all substances at each vapor pressure, and exactly alike for homologous substances, as a consequence of the original law in the symmetrical form (1) or (2).

This was shown to hold for values of both Tdp/dT and r/u by actual computation of these quantities; and the essential features of the secondary law above referred to were given as independent empirical laws, by Ramsay and Young, prior to their announcement of the saturation temperature ratio law.[1] Referring to either of these quantities Ramsay and Young show that it is nearly the same for all substances at normal boiling point (saturation temperature corresponding to 760 mm. Hg vapor pressure) and that the ratio of values for any two given vapor pressures is nearly the same for all substances. These two relations are equivalent to the one given above, that values of $1/T\,dT/dp$, etc., are nearly the same for all substances at each vapor pressure.

Ramsay and Young also extended this approximate law to an exact form similar to (6)[2] giving it as an independent law however, and not as a consequence of the temperature ratio law, as here given. The evidence given by Ramsay and Young in support of the law is really evidence of the validity of the law (1) or (2).

In the paper alluded to, there are given tables from vapor pressure observations, of computed values of $T\,dp/dT$, and it is shown for a number of pairs of substances that the ratio $T_b\,dp/dT_b \div T_a\,dp/dT_a$ for

[1] Phil. Mag., Vol. 20, series 5, 1885, p. 515.
[2] Phil. Mag., Vol. 21, series 5, 1886, p. 136.

various vapor pressures, is a linear function of T_a. This is exactly the law given by (6). In this paper the law is given that the ratio is a linear function of one of the absolute temperatures, but it is not stated as to whether this is the one corresponding to the numerator or denominator of the ratio. However, in all of the examples given, the ratio is shown to be a linear function of the temperature corresponding to the denominator of the form used in the paper, that is, the numerator when the form is as in (6).

LATENT HEAT LAWS.

By means of (7) we may compute u_b/r_b for all vapor pressures for a substance b, from the value for any one vapor pressure, and values of u_a/r_a and T_a for some standard substance a such as water vapor, Then values of either r_b or u_b can be computed if the other is known. As already stated, u is the difference between specific volumes of liquid and vapor at the saturation point and r is the latent heat of vaporization. The law is probably exact although it may be only a close approximation.

A rough approximation of simpler form may be deduced from the preceding considerations. We may write (5) in the form

$$\frac{r_a}{r_b} = c\,\frac{T_b/u_b}{T_a/u_a}.$$

Now u differs from the specific volume in the gaseous state by the specific volume of the liquid, usually a small quantity. In most cases the gaseous volume is nearly that corresponding to the perfect gas laws, and is directly proportional to the absolute temperature and inversely proportional to the molecular weight. Hence T_a/u_a and T_b/u_b are practically proportional to the molecular weights since the pressure is the same for both substances. That is, we have approximately $r_a/r_b = \text{constant} = c\,\gamma_b/\gamma_a$. Here r_a and r_b are latent heats of vaporization for two substances at the same vapor pressure, and γ_a and γ_b are molecular weights. The latent heat ratio is constant for each pair of substances for all vapor pressures. This law will give a general idea of the latent heat of any substance for all pressures from any one value and from known values for the same pressures for some standard substance.

As a further approximation we may substitute from (2) in the last expression, neglecting k since it is always small. This gives

$$\frac{r_a}{r_b} = \frac{T_a}{T_b}\frac{\gamma_b}{\gamma_a},$$

or

$$\frac{r\gamma}{T} = \text{constant},$$

where γ is the molecular weight, or the "normal" density (at standard conditions, 760 mm. Hg and 0° C.), which is proportional to it; r is the latent heat of vaporization, and T is the corresponding saturation temperature. The constant is the same for all substances at a given vapor pressure. There is of course a different constant for each vapor pressure.

The approximate law thus rationally deduced was first given as an empirical law by Trouton,[1] being applied by him only for normal atmospheric pressure however. It is here extended to any pressure whatever.

Effect of Temperature Ratio Law on General Law for Vapor Pressure.

A general relation between pressure and temperature of saturated vapor has long been sought without recognized success. No rational law holding from the supercooled region below the triple point up to the critical point, has ever been formulated. The temperature ratio law here discussed holds for this whole range however, so that it gives a condition which the general vapor pressure equation must satisfy almost if not quite exactly. This condition is that the vapor pressure p must be a function of $(A - B/T)$ where T is absolute saturation temperature and A and B are two constants, different for each substance.[2] Other constants if they occur, are the same for all substances. That is to say, we must have $p = f(A - B/T)$ or $\log p = f(A - B/T)$. This proposition is readily proven by noting that (1) may be written in the form

[1] Phil. Mag., Vol. 18 (series 5), 1881, p. 54.

[2] Aryton and Perry, Phil. Mag., Vol. 21 (series 5), 1886, p. 259.

$$A_2 - \frac{B_2}{T_b} = A_1 - \frac{B_1}{T_a}.$$

Since the constant k is always small, A_1 and A_2 are nearly alike. Hence in the general expression $\log p = f(A - B/T)$ the constant A differs slightly for various substances and is exactly the same for homologous substances.

The mathematical form of statement that p is a function of $A - B/T$ is as follows: Let us first suppose that we are considering various homologous substances, for which A is constant. Then p and $A - B/T$ are each functions of the two independent variables B and T. Since by hypothesis p is also a function of $A - B/T$, we have from the mathematical "condition for functionality"

$$\left(\frac{dp}{dT}\right)_{AB} = -\frac{B}{T}\left(\frac{dp}{dB}\right)_{AT}.$$

In the same way, since A and T may be variable with constant B, we deduce the condition

$$\left(\frac{dp}{dT}\right)_{AB} = \frac{B}{T^2}\left(\frac{dp}{dA}\right)_{BT}.$$

A third equation can be formed, but it is not independent. The general vapor-pressure equation is the integral of these partial differential equations.

DIETERICI'S VAPOR PRESSURE LAWS.

Dieterici has proposed a vapor-pressure law equivalent to

$$7.4\,p\,\frac{T_k}{T}\frac{dT}{dp} = T$$

where T_k is the critical temperature. This gives as the relation between saturation temperatures T_a and T_b of two substances at the same vapor pressure

$$\frac{T_{ak}}{T_{bk}}\frac{\frac{1}{T_a}\frac{dT_a}{dp}}{\frac{1}{T_b}\frac{dT_b}{dp}} = \frac{T_a}{T_b}.$$

By comparison with (4), this law gives the value T_{ak}/T_{bk} for the constant c, so that (1) becomes

$$\frac{1}{T_b} = \frac{T_{ak}}{T_{bk}} \frac{1}{T_a} + k$$

or

$$\frac{1/T_b - k}{1/T_a} = \frac{T_{ak}}{T_{bk}}$$

where T_{ak} and T_{bk} are critical temperatures of the substances a and b.

If we plot reciprocals of absolute saturation temperatures corresponding to the same vapor pressure against each other, as is done in the chart of the previous article,[1] we obtain straight lines, as already shown. According to Dieterici's law the tangents of the angles of these lines with the horizontal will be proportional to the critical temperatures of the substances whose values of $1/T$ are plotted horizontally. Inspection of the chart shows that in a general way this is true, and that the less the angles the lower the critical temperatures. However, quantitative test of the law by measurement of the tangents of the angles of the vapor-pressure lines and comparison with observed critical temperatures shows that there is no approach to proportionality, and that the law is only a very roughly approximate one.

Dieterici's expression for vapor pressure when integrated gives a law of the form

$$\log p = A - \frac{B}{T}.$$

This is the simplest form of law agreeing with the conditions imposed by the temperature ratio law. However, as is well known, such a form does not at all represent observations, so that Dieterici's expressions are not exact.

Vapor Pressure Formulas.

The temperature ratio law enables deduction of a law for vapor pressure of any substance from any of the empirical expressions for water-vapor pressure which can be put in the form $\log p = f(A - B/T)$. This was done in the preceding article for Rankine's law.[2] However this law does not give a very good representation of observations. On the contrary a law for pressure

[1] Phys. Rev., Vol. 16, p. 358.
[2] Phys Rev., Vol. 16, p. 361.

of water vapor of a form suggested by Roche[1] but reconstructed and called by Regnault Formula K[2] gives excellent agreement with observations. The law is

$$p = a\alpha^{\frac{T-253}{1+m(T-253)}}.$$

Regnault gives

$\log \alpha = 0.03833818$ $\log a = \bar{1}.9590414$ $m = 0.004788221$.

This formula agrees very closely with the results of experiments by Regnault and Ramsay and Young[3] and also with experiments at higher temperatures up to the critical point.[4] In the preceding table of saturation temperatures of water vapor a column of values from this Formula K is given. They agree with values computed from methyl alcohol observations within a few tenths of a degree. In fact this formula agrees with any one series of observations as well as the various observers agree among themselves. It probably best represents our present experimental knowledge of water-vapor pressure from below triple point to the critical point.

This formula may be reduced to the general form consistent with the temperature ratio law, and then takes the form (exactly equivalent to the original form given above)

$$\log p = 45.8372 - (0.0264052 - 1.16589/T)^{-1}.$$

Here p is the pressure of water vapor in mm. Hg, and T is the corresponding absolute centigrade saturation temperature. For any other vapor we have as an expression which represents observations accurately

$$\log p = 45.8372 - (A - B/T)^{-1},$$

where A and B are constants for each substance. A is always close to 0.0264052 and has the same value for all substances of a homologous series. In both of these formulas the first constant becomes 44.1236 for pressure in lbs. per sq. in.

There is one class of proposed vapor-pressure formulas which

[1] Memoires de L'Institut, etc., Vol. 10, 1831, p. 227. As given by Roche, the formula does not agree at all with modern observations.

[2] Memoires de l'Institut, etc., Vol. 21, 1847, p. 613.

[3] Phil. Trans., Vol. 183, 1892, p. 111.

[4] Engineering, Vol. 83, January 4, 1907.

cannot be reduced to a form consistent with the temperature ratio law. These have the general form

$$\log p = A + B/T + C \log T.$$

This and similar relations have been deduced rationally by Rankine [1] and Gibbs [2] and others, but so far as the writer's knowledge extends, always for the region at a distance from the critical point, that is, for liquid volume small compared with vapor volume. This form is therefore not rational for the whole region from triple point to critical point. On the contrary the temperature ratio law applies to this whole region, so that concordance with the partial law above is not to be expected.

By empirically selecting the constants to suit, the above form may be applied to the whole region, and fair coincidence is found, since there are three arbitrary constants to choose. However, since this form is empirical and not rational when extended to the whole region, and since it gives no better representation of observations than the Roche law previously discussed, the Roche form is preferable since it is in accord with the temperature ratio law.

Comparison may be made of the temperature ratio law here discussed and the "law of corresponding states." Both laws give a relation between saturation temperatures for two substances, the former for the same vapor pressure, and the latter for vapor pressures bearing the same ratio to the critical pressures. The two laws are therefore distinct.

Reduction of Vapor Pressure Observations.

The form and exactness of the Roche law or "Formula K" suggests a modification of the method used in obtaining the charts of the previous article. We have for any vapor

$$A - B\frac{1}{T} = \frac{1}{45.8372 - \log p}$$

where p is vapor pressure in mm. Hg (constant is 44.1236 for lbs. per sq. in.), and T is the corresponding absolute centigrade saturation temperature. Hence if $1/T$ is plotted against $1/(45.8372 - \log p)$

[1] Phil. Mag., Vol. 31, series 4, 1866, p. 199.

[2] Scientific Papers (Thermodynamics), p. 152, footnote.

from observed values, the points should lie in a straight line, except for observational irregularities. The observations may be smoothed by readings from the straight line best representing the points, or by computation from the formula obtained by use of the numerical values of A and B obtained from the straight line.

The principle at the basis of this method is exactly the same as that used in obtaining the charts of the preceding article. Here however, the ordinates giving the vapor-pressures are obtained by formula instead of from tables of water vapor pressure.

ON THE DENSITY, ELECTRICAL CONDUCTIVITY AND VISCOSITY OF FUSED SALTS AND THEIR MIXTURES.

By H. M. Goodwin and R. D. Mailey.

Contributions from the Research Laboratory of Physical Chemistry No. 16.

THE present paper embodies the results of a research[1] carried out during 1905 and 1906, in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, its object being to obtain data on certain properties of fused salts with such a degree of precision that the following questions might be definitely settled or discussed:

1. The correct values of the specific and equivalent conductance of a number of fused salts which, from the discordance of published data, seemed in need of revision.

2. The temperature coefficient of both the specific and equivalent conductance of these salts.

3. The conductance of mixtures of fused salts with and without an ion in common.

4. The viscosity of pure fused salts and of their mixtures and its variation with the temperature.

5. The validity of Foussereau's Law of the proportionality between fluidity and electrical conductivity.

6. The ionization of fused salts.

During the progress of this investigation certain of the points considered have been made the subject of an independent investigation by Dr. H. T. Kalmus[2] in Professor Lorenz's laboratory in Zürich in which fortunately entirely different methods were employed both for conductivity and viscosity measurements. It is very gratifying

[1] This research was carried out under a grant from the Wm. E. Hale Research Fund, to the trustees of which grateful acknowledgment of the aid furnished by them is hereby made.

[2] Zeit. für phys. Chem., *59*, pp. 17, 244, 1907.

to find that the results of these two independent researches so far as they cover the same ground and permit of comparison are in essential agreement, which greatly increases the weight to be attached to each.

The literature on all matters even remotely bearing upon the question of the conductivity of fused electrolytes has been so exhaustively collected and admirably discussed by Professor Lorenz in his recently published monographs on the Electrolyse Geschmolzener Salze that a recompilation here is superfluous; everyone particularly interested in this branch of electrochemistry may be assumed to have a copy of Lorenz's work at hand. Reference will therefore be made to only those articles which are immediately related to our work.

The results of our research may conveniently be considered under the following subdivisions:

I. Discussion of matters common to all portions of the investigation such as construction of thermostats, measurement of temperature, purification of salts, etc.

II. Density determinations of the pure salts and of their mixtures over a wide range of temperature.

III. Conductivity measurements of the pure salts and of their mixtures over a corresponding range of temperature.

IV. Viscosity measurements of the same salts and mixtures over a corresponding range of temperature.

V. Summary.

I. General Considerations.

(*a*) *Thermostats.* — *Electric Furnaces.* — A preliminary precision discussion of the measurements to be undertaken made evident that the regulation, maintenance and measurement of the temperatures at which the conductivity and viscosity measurements were made was of fundamental importance, since the temperature coefficient of these properties of fused salts although less than the temperature coefficient of their corresponding aqueous solutions, is still large, in some cases over one per cent. per degree. There is no doubt that much of the discrepancy between the results obtained by previous investigators is due to inaccuracy in their temperature measurements. We therefore devoted considerable time to devising baths or thermostats in which temperatures up to 500° C. could be maintained

constant to a few tenths of a degree as long as desired, and to the measurement of these temperatures to the same degree of precision.

Three different types of thermostats or furnaces were therefore used in the progress of our work for maintaining the necessary temperatures for the density, conductivity, and viscosity measurements respectively.

The *first* was a vertical platinum resistance furnace of the usual type, the fire-clay cylinder on which the platinum was wound being 7.5 cm. in diameter and 25 cm. high, and packed in magnesium oxide. This furnace was used for heating the crucible containing the fused salt in the density measurements.

The *second* was an air-bath surrounded by a molten metal bath kept at constant temperature by electrical heating.

The *third* was a fused nitrate bath into which the viscosity apparatus was directly immersed.

The first of these furnaces needs no special description. The second contains some features worth mentioning and is shown in vertical section in Fig. 1.

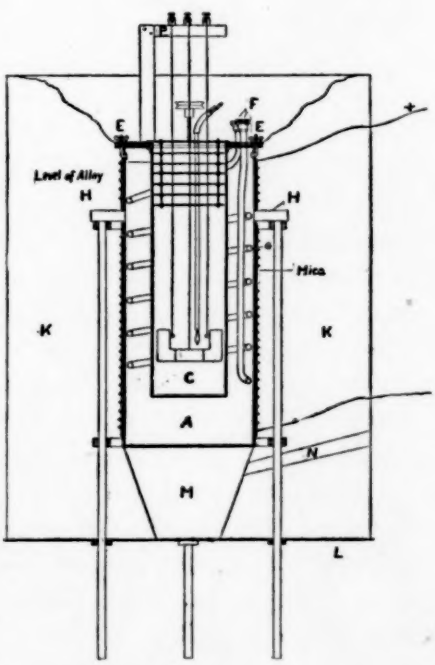


Fig. 1.

The inner air bath *C*, in which the conductivity cell was suspended, was 32 cm. deep and elliptical in cross-section, the major and minor axes of the ellipse being about 8.5 and 2.5 centimeters respectively. This cross-section was chosen so as to reduce the air space about the conductivity cell to a minimum. A deep bath was used in order that radiation from the top might not effect the temperature in the neighborhood of the conductivity cell. To further reduce the loss of heat to a minimum, the top of

the air-bath was closed with a series of seven mica covers separated 1 cm. from one another. The necessary holes for the introduction of the thermo-electric junction and lead wires to the cell were cut through these covers which served not only to insulate but also to hold them in position in the furnace.

The inner cylinder *C* was fitted into a circular iron plate which formed the cover to the metal bath *A*. This cover was held in place by wing nuts *EE*. The iron pot *A* containing the metal was about 15.5 cm. in diameter and 38 cm. deep. It was filled to within 3 or 4 centimeters of the top with an alloy consisting of 30 per cent. lead and 70 per cent. tin, which melted at about 180° C. The molten mass was stirred by means of two screw propellers, not shown in the figures placed one on each side of the air-bath, *C*. These propellers were driven in opposite directions by an electric motor, and a thorough circulation of the bath was thus secured.

The furnace was heated by electricity. On the outside of *A* were wound 93 turns of No. 14 B. and S. nickel-steel wire, insulated from the iron by a layer of asbestos cloth and mica. This winding had a resistance of 22 ohms at room temperature and a resistance of about 28 ohms at 450° C. The current was regulated by an external rheostat; the energy absorbed was about 400 watts at 400° C. For lowering the temperature of the furnace, four meters of steel tubing, 7 mm. in diameter, were coiled about the inside wall of the pot. The ends *F* were brought out at the top of the furnace and one connected to the waste pipe, the other to a three-way cock by means of which air or water could be sent through the coil as desired. To reduce the violence of the vaporization within the tube when water was introduced, the outside of the tube was wound with a thin layer of asbestos. The primary object of this coil was to cool the bath rapidly when necessary, but it also proved very convenient in regulating the temperature.

For heat insulation an 11 cm. jacket *K* of asbestos fiber surrounded the whole apparatus, except the top. The fiber was held in place at the sides and bottom by asbestos paper. In the bottom an opening *M* was left with the chimney *N* so that the bath might be heated in part by a Bunsen burner when desired. The whole furnace was supported by lugs *H* which rested on an iron tripod.

The conductivity cell was suspended in the heater from a brass frame P mounted on the cover. At the top of this frame were three binding posts insulated from each other and from the furnace by hard rubber. From these posts the cell was suspended by platinum wires.

The temperature regulation in this furnace was effected by hand. When a desired temperature was reached the current was reduced by means of the rheostat until the heat supplied just balanced the radiation; the temperature could be held constant as long as desired to 0.2° C. up to 500° and over, by a slight variation of the current. Owing to the very large mass of the metal bath the fluctuations in temperature were very slow. If the temperature was found to be a little too high small quantities of air, blown through the cooling tube brought it back to the desired value. When it was necessary to cool the furnace any considerable amount, water was blown through the cooling tube. By this means the temperature could be reduced from 450° C. to 40° C. in 30 minutes, while by ordinary radiation the furnace cooled from 450° C. to only 100° C. in 15 hours.

The third thermostat used in connection with our viscosity investigation consisted of a bath of fused sodium and potassium nitrate. This was contained in an iron pot 23 cm. high and 15.5 cm. in diameter, the outside of which was wound with No. 14 B. and S. nickel-steel wire as in the type of furnace just described. The bath was heat insulated by asbestos fiber — twelve inches thick on the sides and seventeen inches on the bottom. An opening was left at the bottom so that the bath could also be heated by a Bunsen flame. This was used to keep the bath in a state of fusion, while the regulation of temperature was effected by the heating coil. Into this bath the viscosity apparatus was directly immersed.

(*b*) *Measurement of Temperature.* — All temperatures were measured by means of a carefully calibrated platinum-rhodium couple which gave about 8 microvolts per degree centigrade. The part of the couple inside the furnace was encased in a clay tube to within 3 or 4 centimeters of the junction. Outside the furnace the wires were covered by small rubber tubing. The cold junction, *i. e.*, where the copper leads joined the platinum and rhodium wires, was arranged as follows. Each soldered connection was pushed through

a small glass tube the lower end of which was then filled with sealing wax. These tubes were held in place in a test-tube by means of the cork stopper. The test-tube was filled with an insulating oil, and when measurements were in progress was packed in finely chopped ice in a 2-liter felt jacketed thermostat. By this means the cold junction was kept at a constant known temperature.

The thermo-electric force corresponding to any temperature of the hot junction was measured in a special slide wire potentiometer, in conjunction with a very sensitive low resistance d'Arsonval galvanometer as indicating instrument. The arrangement of apparatus is shown in Figs. 2 and 3. In Fig. 2 the slide-wire, a, is connected in

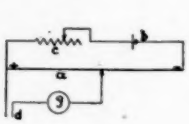


Fig. 2.

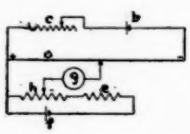


Fig. 3.

series with a storage cell, b, of large capacity, and c, a variable resistance; d is the couple, and g the galvanometer. When a balance point a_c, as indicated by no deflection of the galvanometer has been obtained, without changing the adjustment of a, b or c, the arrangement shown in Fig. 3 is thrown into the circuit in place of the thermal junction. Here e is a 20,000-ohm coil, h a variable resistance, and f a cadmium cell of special design. By adjusting h, a fraction of the voltage of the cadmium cell may be tapped off of such magnitude as will give a balance a_s on the slide-wire very near to the balance point obtained with the couple. From these readings the E.M.F. of the couple in terms of the E.M.F of the standard cell may be calculated at once. If we let

ϵ_c = E.M.F. of couple,
ϵ_s = E.M.F. of standard cell,
a_c = reading on slide-wire with couple,
a_s = reading on slide-wire with standard,
R_h = resistance unplugged in h,
R_e = 20,000 ohms,
R_f = internal resistance of standard cell,

the E.M.F. of the couple is given by the formula

$$\epsilon_c = \epsilon_s \frac{R_h}{R_c + R_h + R_f} \frac{a_c}{a_s}.$$

In order that this calibration might be reliable a special form of standard cadmium[1] cell shown in Fig. 4 was used. The large electrode area gave a low internal resistance, about 20 ohms, and also prevented a change in E.M.F. due to polarization when the slight current was taken from it during a measurement. A low internal resistance was desirable on account of the variation in resistance with change in temperature (2.5 per cent. per 1° C.). To make sure that the E.M.F. of the cell remained constant, it was from time to time compared with a group of six Weston standard cells, in the standardizing laboratory.

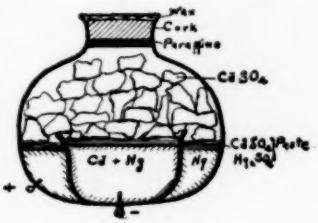


Fig. 4.

Thermo-electric disturbances in the various parts of the apparatus were eliminated by introducing the usual compensating device in the galvanometer circuit. A diagram of the complete arrangement of circuits as used in our measurements is given in Fig. 5.

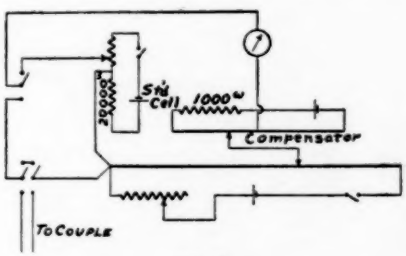


Fig. 5.

Calibration of Thermal Junction.

The thermo-electric couple was calibrated at four fixed points and from these data curves connecting temperature and electromotive force were plotted on a large scale (100 cm. square). The points taken were the boiling temperatures of water, naphthalene, benzophenone and sulphur. Distilled water was boiled in a steam-jacketed copper boiler such as is used for mercurial thermometer calibration, and the temperature of the steam calculated from the barometric pressure at time of observation.

[1] Physiko-chemische Messengen Ostwald-Luther, p. 361.

The naphthalene and benzophenone points were determined in upright boilers 50 cm. long by 5 cm. in diameter. The outside was covered with pipe covering, and concentric screens were placed inside to prevent radiation from the walls to the junction. The junction was suspended in the vapor space inside the screen, through a glass cover, glass being used in order that the level of the vapor could be observed and kept at the proper height in the boiler. A mica hood was placed just above the junction to prevent condensed vapor from running down on the couple. The temperature of the vapor was calculated from the barometric pressure at the time of measurement and the data given by Jacquerod and Wassmer,[1] on the boiling points of naphthalene and benzophenone.

For the sulphur point a boiler was used similar to that described above except that an additional screen was placed between the surface of the liquid sulphur and the junction, as recommended by Callender and Griffiths.[2] A mica hood was placed over the couple as in the other cases. The couple was suspended in the vapor to a depth of 22 cm. which was equal to the length introduced inside the furnace during the conductivity measurements.

The chemicals used for these vapor baths were from Kahlbaum. The naphthalene and benzophenone were recrystallized from alcohol. The sulphur was used as it came, since Callender and Griffiths used it in this way and we wished to reproduce the conditions of their experiments as nearly as possible and use the boiling point obtained by them.

The values which we used for our fixed joints are given below.

Substance.	Barometer.	Temperature.	dt/dp per mm.
Naphthalene	760 mm.	217.68° C.	0.058°
Benzophenone	760	305.44	0.062
Sulphur	760	444.52	0.088

(*c*) *Preparations.* — In selecting salts for our investigation we required several whose melting point permitted them to be investigated over approximately the same range of temperature and which

[1] Jour. de Chim. et de Phys., II., 52–78, 1904.
[2] Phil. Trans., *182* (A), pp. 119-158, 1891.

at the same time were univalent in order that the mutual effect of their dissociation might be as simple as possible. As the apparatus to be described was designed to give the precision desired only up to about 500° our choice was necessarily limited.

We chose, therefore, in the first instance, sodium and potassium nitrates, as fulfilling the above conditions, first, because existing data on these salts certainly needed revision and second, because the only existing viscosity measurements on fused salts (which we felt also needed confirmation) were on these two salts. To these we afterwards added lithium nitrate, silver nitrate, and silver chlorate, the last being chosen as a univalent salt of proper melting point which possessed no ion in common with the alkali nitrates.

These salts were, with the exception of silver chlorate, obtained from Baker & Co. and marked C.P. They were purified by repeated recrystallization until by the spectroscope practically all foreign metals were proved to be absent. They were then fused, cooled and ground to a powder and kept in a desiccator or glass stoppered bottle.

The silver chlorate was prepared by adding pure barium chlorate to a saturated solution of silver sulphate, filtering, and partially evaporating the filtrate. Upon cooling silver chlorate separated out in beautiful crystals. On account of the slight solubility of silver sulphate this process was somewhat tedious as many liters of filtrate had to be evaporated.

The mixtures were prepared by weighing out the calculated proportions of the two component salts (these having been previously fused), fusing the two together, cooling, and regrinding the mass in a mortar to a fine power.

Freezing Point of the Salts and their Mixtures.

Although data on the melting or freezing point of most of the salts which we investigated are given in Landolt & Börnstein's tables, we determined the value for our preparations, as this involved little extra work and served to indicate the purity of the salts.

For each determination not less than 15 c.c. of fused salt was used; this was contained in a platinum crucible, placed in the platinum resistance furnace. The melt, which was continuously stirred,

was allowed to cool slowly, and the temperature at which the rate of cooling became zero was taken as the freezing point.

All temperatures were determined with the thermo-electric junction. In the case of the mixtures small crystals of the solid mixture were dropped into melt to prevent under-cooling. The values given in the following table are the mean of several determinations together with their average deviations. Our values the for alkali nitrates are about three degrees lower than those obtained by Carveth using a mercury thermometer, an amount greater than the deviations among the measurements themselves. On the other hand, our values on the mixtures of sodium and potassium nitrates agree very well with the values found by him.

Freezing Point Data.

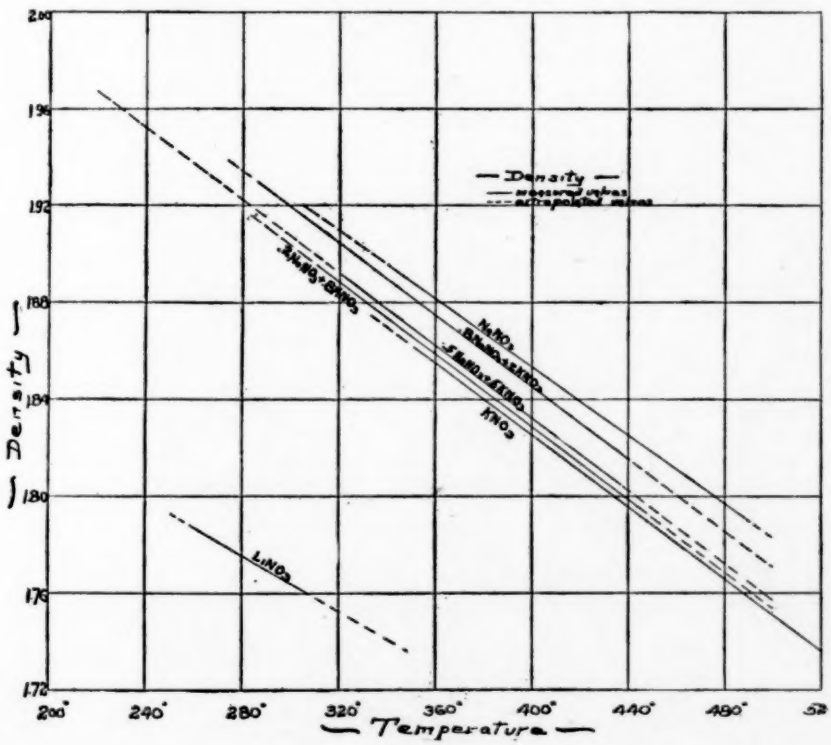
Salt.	G. and M.	Carnelley.	Carveth.
KNO_3	333.7 ± 0.0	339.0	337
$NaNO_3$	305.6 ± 0.4	319.0	308
$LiNO_3$	250.2 ± 0.5	264	253
$AgClO_3$	215.0 ± 1.5	—	—
$AgNO_3$	218.0 ± 1.0	217 ± 2	—
0.2 KNO_3 + 0.8 $NaNO_3$	274 ± 2	—	273
0.5 KNO_3 + 0.5 $NaNO_3$	220 ± 0.5	—	221
0.8 KNO_3 + 0.2 $NaNO_3$	284.0 ± 1.5	—	285

II. Measurement of Density.

The density determinations were made with a modified form of Westphal balance, in which the sinker used was constructed of fused silica for densities less than 2.6, and with a delicate analytical balance from one pan of which a platinum ball was suspended, for greater densities. Fused silica is admirably adapted for a sinker, since its change of volume over wide ranges of temperature is very slight and easily calculated from its known coefficient of expansion. Moreover, its density being low, it is very sensitive to changes in the density of the liquids in which it is suspended. The volume of the silica sinker which we used was about 11 c.c., that of the platinum ball 9 c.c. In constructing the set of Westphal weights the following method was used. The balance was adjusted for equilibrium with the sinker freely suspended at the end of the

balance arm. The sinker was then suspended in distilled water at 4° C. and its loss in weight accurately determined. A set of decimal weights of the usual Westphal form was then constructed with this weight as a unit. With such a series of weights, densities up to 2.6 could be measured to the third place of decimals, while the fourth place could be estimated by observing the swing of the balance. The only correction to be applied to the observed densities was for the expansion of the sinker for which $\alpha = 0.0000021$ [1] for vitreous quartz; for the platinum ball $\alpha = 0.00002668$.[2]

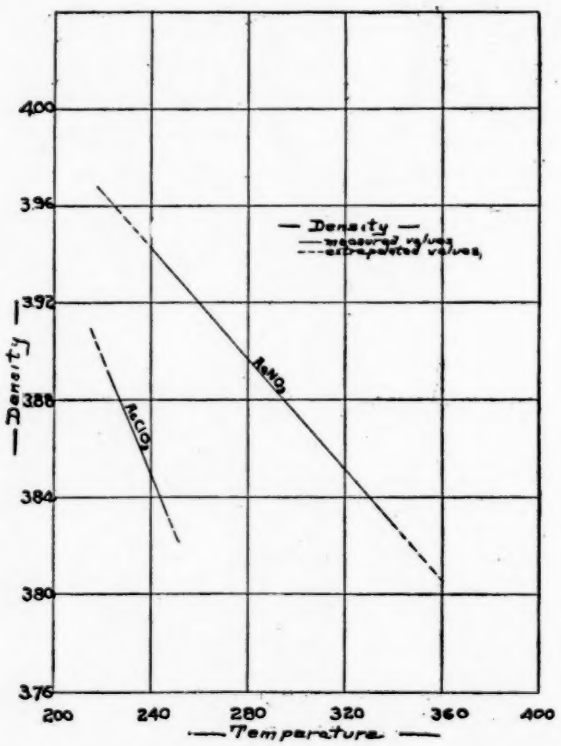
In measuring the densities of the fused salts, the balance was placed upon a table over the platinum resistance furnace so that the sinker, suspended by fine platinum wire, hung in a cylindrical platinum crucible placed inside the furnace. This crucible



Plot I.

[1] C. R., *130*, p. 1703, 1900.
[2] Ann. der Physik, *2*, p. 509, 1900.

contained the salt whose density was to be determined. The temperature was measured with a thermo-couple, the junction being placed in the fused salt along with, but not touching, the sinker. By varying the temperature of the furnace, rapid and accurate measurements of the density of the fused salts could be made at different temperatures with ease. Independent determinations agreed well within 0.1 per cent.

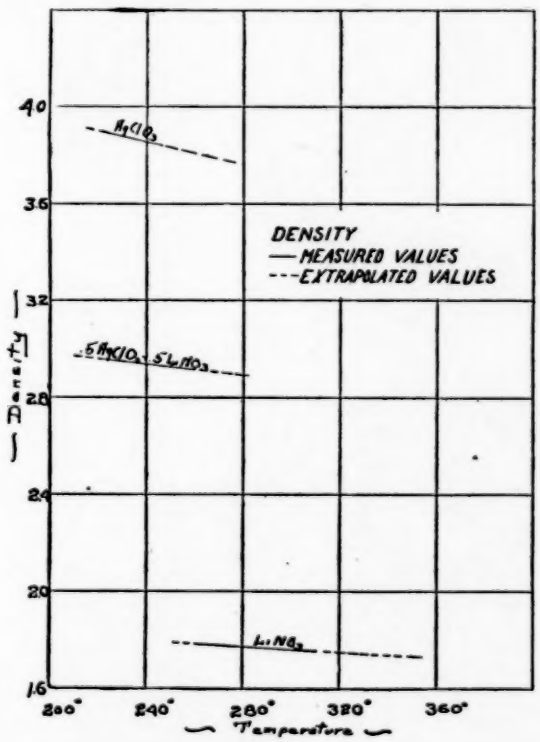


Plot II.

The observed data on the pure salts are given in Tables I. to V. and those on the mixtures in Tables VI. to IX. respectively. These data were plotted, the best representative line for each salt or salt mixture found, and its equation determined. The density-curves are shown on a reduced scale in Plots I., II. and III. The dotted portion of a line represents an extrapolation beyond the actual observations. The equations expressing the density as a function

of the temperature are in all cases linear over the range of temperature studied, the agreement between the observed values and values computed from these formulæ being better than 0.1 per cent.

In Tables I*a* to IX*a* are given the values of the density for each salt and salt mixture at intervals of ten degrees, the values being interpolated directly from the original plots. The corresponding values of the specific volume, $S = 1/D$, are given in column three.



Plot III.

The values of the molecular volume $\phi = MS$ have also been computed for the pure salts and are given in column four, Tables I*a* to V*a*.

Tables VI*a* to IX*a* contain in addition to values of the density and specific volume of the several mixtures the values of the specific volume of the mixture computed from the respective specific volumes of the components. The values below 350° are calculated

from the densities which the pure salts would have if they could be cooled to the temperatures in question without solidifying. These were computed from the formulae given below, Tables I. and II. respectively. The computed specific volumes are given in column four, and the differences between observed and computed values are given in column five. It will be seen that in every case, except the last (Table IX*a*), mixture of the salts is accompanied by a slight

TABLE I.

Density of $NaNO_3$ Referred to H_2O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
342.6	1.893	1.893	±.000
400.8	1.852	1.852	±.000
433.6	1.828	1.829	+.001
452.4	1.814	1.814	±.000
491.5	1.789	1.789	±.000

$D_t = 1.853\,[1 - 0.000379\,(t - 400)]$.

TABLE I*a*.

Specific and Molecular Volume of $NaNO_3$. Molecular Weight: $M = 85.09$.

Temperature.	Density. D.	Specific Volume. S.	Molecular Volume. $\phi = MS$.
305 M.P.	1.920	0.5208	44.32
320	1.909	0.5240	44.57
330	1.902	0.5258	44.74
340	1.895	0.5278	44.90
350	1.888	0.5299	45.07
360	1.880	0.5319	45.26
370	1.873	0.5340	45.43
380	1.866	0.5361	45.60
390	1.859	0.5382	45.77
400	1.852	0.5400	45.95
410	1.845	0.5417	46.12
420	1.838	0.5444	46.29
430	1.831	0.5461	46.47
440	1.824	0.5481	46.65
450	1.817	0.5500	46.83
460	1.810	0.5525	47.01
470	1.803	0.5545	47.19
480	1.796	0.5566	47.38
490	1.789	0.5586	47.56
500	1.782	0.5611	47.75

TABLE II.

Density of KNO_3 Referred to H_2O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
352.0	1.858	1.861	+.003
365.0	1.853	1.852	−.001
372.3	1.847	1.846	−.001
391.5	1.832	1.832	±.000
404.6	1.823	1.823	±.000
421.4	1.809	1.810	+.001
427.8	1.804	1.805	+.001
443.9	1.794	1.794	±.000
451.0	1.785	1.788	+.003
468.0	1.775	1.776	+.001
497.0	1.756	1.754	−.002
504.0	1.749	1.749	±.000
535.0	1.726	1.726	±.000
553.9	1.712	1.712	±.000
554.0	1.714	1.712	−.002
564.0	1.706	1.705	−.001

$$D_t = 1.826\,[1 - 0.000405\,(t - 400)].$$

TABLE II*a*.

Specific and Molecular Volume of KNO_3. Molecular Weight: $M = 101.18$.

Temperature.	Density. D.	Specific Volume. S.	Molecular Volume. $\phi = MS$.
333.7 M.P.	1.875	0.5335	53.96
340	1.870	0.5348	54.11
350	1.863	0.5368	54.31
360	1.856	0.5390	54.51
370	1.848	0.5407	54.75
380	1.841	0.5431	54.96
390	1.833	0.5456	55.20
400	1.826	0.5474	55.41
410	1.818	0.5497	55.66
420	1.811	0.5521	55.87
430	1.804	0.5542	56.08
440	1.796	0.5566	56.34
450	1.789	0.5586	56.56
460	1.782	0.5611	56.78
470	1.774	0.5636	57.05
480	1.767	0.5657	57.39
490	1.759	0.5682	57.52
500	1.752	0.5707	57.75
510	1.745	0.5729	57.98

TABLE III.

Density of $LiNO_3$ Referred to H_2O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
259.9	1.788	1.788	±.000
267.3	1.785	1.783	—.002
269.9	1.782	1.782	±.000
281.3	1.775	1.775	±.000
281.5	1.775	1.775	—.001
297.0	1.766	1.766	±.000
308.8	1.760	1.760	±.000

$$D_t^1 = 1.776\,[1 - 0.000322\,(t - 280)].$$

TABLE III*a*.

Specific and Molecular Volume of $LiNO_3$. Molecular Weight: $M = 69.07$.

Temperature.	Density. D.	Specific Volume. S.	Molecular Volume. $\phi = MS$.
250 M.P.	1.794	0.5573	38.50
260	1.788	0.5590	38.63
270	1.782	0.5611	38.76
280	1.776	0.5629	38.89
290	1.771	0.5646	39.00
300	1.765	0.5664	39.13
310	1.759	0.5682	39.27
320	1.753	0.5703	39.40
330	1.747	0.5722	39.54
340	1.742	0.5741	39.65
350	1.736	0.5760	39.79

TABLE IV.

Density of $AgNO_3$ Referred to H_2O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
239.0	3.944	3.941	—.003
244.5	3.935	3.935	±.000
254.0	3.926	3.924	—.002
262.0	3.913	3.915	+.002
306.5	3.864	3.866	+.002
309.0	3.864	3.863	—.001
342.0	3.829	3.826	—.003

$$D_t = 3.8734\,[1 - 0.000287\,(t - 300)].$$

TABLE IV*a*.

Specific and Molecular Volume of $AgNO_3$. Molecular Weight: $M = 169.97$.

Temperature.	Density. D.	Specific Volume. S.	Molecular Volume. $\phi = MS$.
218 M.P.	3.964	0.2522	42.88
230	3.952	0.2531	43.01
240	3.940	0.2538	43.14
250	3.929	0.2545	43.26
260	3.918	0.2552	43.38
270	3.907	0.2559	43.50
280	3.896	0.2567	43.63
290	3.885	0.2573	43.75
300	3.873	0.2582	43.89
310	3.863	0.2589	44.00
320	3.851	0.2596	44.14
330	3.840	0.2604	44.26
340	3.829	0.2612	44.39
350	3.818	0.2619	44.52
360	3.807	0.2627	44.69

TABLE V.

Density $AgClO_3$ Referred to H_2O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
223.0	3.872	3.874	+.002
230.3	3.861	3.861	±.000
231.5	3.859	3.859	±.000
247.0	3.831	3.832	+.001

$$D_t = 3.8619\,[1 - 0.000451\,(t - 230)\,].$$

TABLE V*a*.

Specific and Molecular Volumes of $AgClO_3$. Molecular Weight: $M = 191.37$.

Temperature.	Density. D.	Specific Volume. S.	Molecular Volume. $\phi = MS$.
200	3.934	0.2452	48.65
210	3.897	0.2566	49.11
215 M.P.	3.888	0.2572	49.22
220	3.879	0.2578	49.33
230	3.862	0.2589	49.55
240	3.844	0.2601	49.78
250	3.827	0.2613	50.00

expansion, *i. e.*, the observed specific volume is greater than that which the mixture would possess did no change in the volume of the components occur on mixing. Although this difference is small, it is unmistakable, being greater than the limits of experi-

TABLE VI.

Density of Mixture of 2 *Mols* KNO_3 + 8 *Mols* $NaNO_3$ *Referred to* H_2O *at* 4°C.

Temperature.	Density Observed.	Density Computed.	Difference.
286.2	1.927	1.928	+.001
332.4	1.894	1.894	±.000
363.4	1.870	1.870	±.000
412.0	1.835	1.835	±.000
440.8	1.816	1.814	—.002

$$D_t = 1.844\ [1 - 0.000400\ (t - 400)].$$

TABLE VI*a*.

Specific Volume of 2 *Mols* KNO_3 + 8 *Mols* $NaNO_3$.

Temperature.	Density. *D.*	Specific Volume. *S.*	Specific Volume Computed.	Difference.
274 M.P.	1.937	0.5163	0.5162	0.0001
290	1.925	0.5195	0.5194	0.0001
300	1.918	0.5214	0.5213	0.0001
310	1.910	0.5236	0.5232	0.0004
320	1.903	0.5255	0.5252	0.0003
330	1.896	0.5274	0.5271	0.0003
340	1.888	0.5297	0.5292	0.0005
350	1.881	0.5317	0.5313	0.0004
360	1.874	0.5336	0.5333	0.0003
370	1.866	0.5359	0.5353	0.0006
380	1.859	0.5379	0.5375	0.0004
390	1.852	0.5400	0.5397	0.0003
400	1.844	0.5423	0.5415	0.0008
410	1.837	0.5443	0.5433	0.0010
420	1.830	0.5464	0.5459	0.0005
430	1.823	0.5485	0.5477	0.0008
440	1.815	0.5509	0.5498	0.0011
450	1.808	0.5532	0.5517	0.0015
460	1.801	0.5552	0.5542	0.0010
470	1.793	0.5576	0.5563	0.0013
480	1.786	0.5591	0.5584	0.0007
490	1.779	0.5618	0.5605	0.0013
500	1.771	0.5645	0.5630	0.0015

mental error. Inspection of the column of differences in the tables further shows:

1. The difference between observed and computed values tends to increase slightly with rising temperature.

2. The difference resulting from mixing 2 mols KNO_3 with 8 mols $NaNO_3$ is less, than that resulting from mixing 2 mols $NaNO_3$ with 8 mols KNO_3.

TABLE VII.

Density of Mixture of 5 *Mols* KNO_3 + 5 *Mols* $NaNO_3$ *Referred to* H_2O *at* 4° *C.*

Temperature.	Density Observed.	Density Computed.	Difference.
320.8	1.891	1.891	±.000
365.0	1.858	1.858	±.000
414.5	1.821	1.821	±.000
437.0	1.804	1.804	±.000

$$D_t = 1.832\,[1 - 0.000408\,(t - 400)].$$

TABLE VII*a*.

Specific Volume of 5 *Mols* KNO_3 + 5 *Mols* $NaNO_3$.

Temperature.	Density. *D.*	Specific Volume. *S.*	Specific Volume Computed.	Difference.
220 M.P.	1.967	0.5084	0.5078	0.0006
300	1.907	0.5245	0.5232	0.0007
310	1.899	0.5268	0.5251	0.0017
320	1.892	0.5286	0.5272	0.0014
330	1.884	0.5309	0.5291	0.0018
340	1.876	0.5333	0.5313	0.0020
350	1.869	0.5353	0.5334	0.0019
360	1.862	0.5371	0.5355	0.0016
370	1.854	0.5395	0.5374	0.0021
380	1.847	0.5410	0.5396	0.0014
390	1.839	0.5441	0.5419	0.0022
400	1.832	0.5459	0.5437	0.0022
410	1.824	0.5481	0.5457	0.0024
420	1.817	0.5500	0.5483	0.0017
430	1.809	0.5524	0.5502	0.0022
440	1.802	0.5549	0.5524	0.0025
450	1.794	0.5573	0.5543	0.0030
460	1.786	0.5597	0.5568	0.0029
470	1.779	0.5618	0.5591	0.0027
480	1.771	0.5646	0.5612	0.0034
490	1.764	0.5668	0.5634	0.0034
500	1.757	0.5689	0.5659	0.0030

3. The difference is a maximum for equimolecular mixtures of these two salts, becoming for this mixture as great as 0.5 per cent.

4. The specific volume of sodium and of potassium nitrates in mixtures of the two salts at temperatures below those at which the pure salts can exist in the liquid state, can be calculated by a linear extrapolation of their respective densities below their melting point.

5. Mixtures of silver chlorate and lithium nitrate show a decided

TABLE VIII.

Density of Mixture of 8 *Mols* $KNO_3 + 2$ *Mols* $NaNO_3$ *Referred to* H_2O *at* 4° *C.*

Temperature.	Density Observed.	Density Computed.	Difference.
312.6	1.894	1.893	—.001
383.6	1.840	1.840	±.000
445.8	1.793	1.793	±.000

$$D_t = 1.828\,[1 - 0.000407\,(t - 400)].$$

TABLE VIII*a*.

Specific Volume of 8 *Mols* $KNO_3 + 2$ *Mols* $NaNO_3$.

Temperature.	Density. *D.*	Specific Volume. *S.*	Specified Volume Computed.	Difference.
284 M.P.	1.914	0.5226	0.5218	0.0008
300	1.902	0.5258	0.5251	0.0007
310	1.896	0.5276	0.5270	0.0006
320	1.889	0.5296	0.5292	0.0004
330	1.881	0.5316	0.5311	0.0005
340	1.873	0.5340	0.5334	0.0006
350	1.866	0.5361	0.5354	0.0007
360	1.858	0.5385	0.5375	0.0010
370	1.851	0.5402	0.5394	0.0008
380	1.843	0.5424	0.5417	0.0007
390	1.835	0.5451	0.5441	0.0010
400	1.828	0.5467	0.5459	0.0008
410	1.820	0.5495	0.5481	0.0014
420	1.812	0.5518	0.5505	0.0013
430	1.805	0.5538	0.5526	0.0012
440	1.797	0.5562	0.5549	0.0013
450	1.790	0.5587	0.5569	0.0018
460	1.782	0.5611	0.5594	0.0017
470	1.774	0.5636	0.5618	0.0018
480	1.767	0.5657	0.5639	0.0018
490	1.759	0.5682	0.5663	0.0019
500	1.752	0.5707	0.5688	0.0019

contraction in volume upon mixing, the contraction amounting in the case of equimolecular quantities to 1.6 per cent. In this case it is to be noted that the two components contain no common ion as in the preceding mixtures of sodium and potassium nitrate.

TABLE IX.

Density of Mixture of 5 *Mols* $AgClO_3 + 5$ *Mols* $LiNO_3$ *Referred to* H_2O *at* 4° *C.*

Temperature.	Density Observed.	Density Computed.	Difference.
223.5	2.953	2.953	±.000
230.7	2.946	2.946	±.000
244.1	2.930	2.931	+.001
251.1	2.925	2.924	—.001
259.8	2.914	2.914	±.000

$D_t = 2.936\ [1 - 0.000366\ (t - 240)]$.

TABLE IX*a*.

Specific Volume of 5 *Mols* $AgClO_3 + 5$ *Mols* $LiNO_3$.

Temperature.	Density. *D.*	Specific Volume. *S.*	Specific Volume Computed.	Difference.
210	2.968	0.3369	0.4037	—0.0668
220	2.957	0.3382	0.4052	—0.0670
230	2.946	0.3394	0.4065	—0.0671
240	2.936	0.3406	0.4080	—0.0674
250	2.925	0.3419	0.4095	—0.0676

The values of the specific and molecular volumes given in the above tables will be made use of in the computation of the molecular conductance and fluidity of the salts, which properties will be considered in the following divisions of this paper.

(*To be continued.*)

THE VAPOR PRESSURE OF CARBONIC ACID.

BY JOHN ZELENY.

IN the May number of the PHYSICAL REVIEW Professor du Bois calls attention to a possible difference in the cryogenic properties of the snow obtained from commercial carbonic acid of different manufacture. He states that in their experiments for getting the vapor pressure of solid carbonic acid, he and Wills[1] used commercial gas which had been made from coke and contained at least 99.5 per cent. of carbonic acid with possible traces of air, water and grease.

As the results of some similar determinations made in this laboratory were published in this journal,[2] I wish to make some additional statements about the nature of the gas used. In the first place the gas coming from the cylinder was found to be perfectly odorless. In the experiments performed by Smith and me for determining the vapor pressure of liquid and solid carbonic acid at low temperatures, the gas was freed from its admixed air by allowing it to flow into a glass tube, the lower end of which was immersed in liquid air. The carbonic acid gradually froze at the bottom of this tube, while the air escaped. The gas obtained from this solid carbonic acid was almost completely absorbed by KOH, the residue being approximately one fortieth of one per cent.

I have since written to the company which supplied the gas, and they inform me that the gas was collected from fermenting vats and then passed in succession through four purifiers, each twenty feet high, the materials of which were copiously sprayed with water. The gas was then passed through calcium chloride on the way to the compressor. They inform me, further, that as shown by daily tests made at the factory, the gas obtained by this process is exceptionally pure, containing only a small amount of air and no traces of any vegetable substances.

[1] du Bois and Wills, Verh. der D. Phys. Gesell., I., p. 168.

[2] J. Zeleny and R. H. Smith, PHYS. REV., 24, p. 42; J. Zeleny and A. Zeleny, PHYS. REV., 23, p. 308.

It would thus appear that the gas we used was of good purity. The effect of any impurity upon the vapor pressure of a solid is somewhat uncertain, depending not only upon its nature but also upon whether it is just mechanically mixed with the substance or whether it forms a solid solution with it.

The experiments which I carried out with A. Zeleny show that neither alcohol nor ether added to carbonic acid snow so as to form a thick mush with it, affects its vapor pressure appreciably over a wide range of temperatures. The temperature-vapor pressure curve obtained with these mixtures, the temperature at any pressure being acquired by the evaporation of the carbonic acid, was found to agree well with the curve obtained by Smith and me where the pure solid carbonic acid was maintained at different temperatures by the aid of liquid air.

We used the temperature of a mixture of alcohol and carbonic acid as determined by Holborn,[1] in Berlin, with a hydrogen thermometer as one of the calibration points for our thermo-element, and the point on the calibration curve was in harmony with the other points used. The results obtained with our carbonic acid for the vapor pressure of the liquid up to 25 atmospheres pressure and for the solid for pressures above one atmosphere agree well with the results obtained by Kuenen and Robson[2] in Scotland. Such agreements point to the absence of deleterious impurities.

I agree with Professor du Bois that it is difficult to get the value of $dP/d\theta$ accurately at 76 cm. pressure from the experimental curves. The value of the tangent being in the neighborhood of 6, a change of 1° in the inclination of the curve at the desired place makes a change of about 10 per cent. in the tangent. Still, the error in drawing the curve with its true inclination is apt to be less where the experimental points extend a considerable distance to each side of the 76 cm. as they did in the case of Smith and myself, than where they end close to the 76 cm. point.

THE PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
July 20, 1907.

[1] Holborn, Annal. der Physik, 6, p. 245.

[2] Kuenen and Robson, Phil. Mag. (6), 3, p. 149.

A TRANSPORTABLE FORM OF STANDARD CELL.

BY RALPH E. DELURY.

THE ordinary or H-form of cell and also its modification, the Λ-form, possess the disadvantage that they are not transportable. Rough handling will cause the contents of the two legs to mix thus destroying the cell as a standard. In the cell described below, the contents cannot mix even though the cell be inverted or shaken. A glance at Fig. 2 will show the shape of the cell. It may be made as follows:

Take a piece of tubing *A*, Fig. 1, of suitable thickness, 15 or 20 cm. long and 1.5 to 2.5 cm. in diameter. Take another piece *B*,

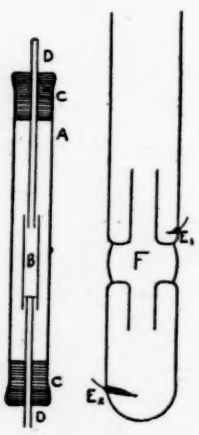


Fig. 1.

Fig. 2.

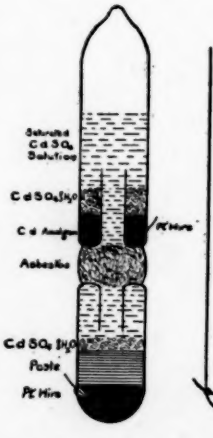


Fig. 3.

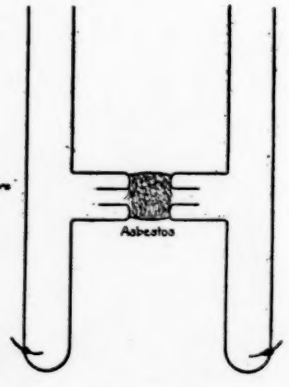


Fig. 4.

6 to 8 cm. long and 0.5 to 1.0 cm. in diameter. Place *B* inside *A* and insert in the ends of *A* tight-fitting corks *C* through which pass the small tubes *D* one of which is open, the other sealed. Adjust the lengths of the tubes *D* so that they enter *B* just enough to hold it co-axial with *A*. The whole is held horizontally and is rotated in the small pointed flame of a blowpipe — or better in the flames of two blowpipes pointing into one another. The tube *A* is melted

in a narrow band nearly opposite the middle of B. At this point A adheres to B and after the tubes are thoroughly fused together they are blown out. While the tube is still warm the platinum wire E_1 is fused in above the bulb of the cell, in the usual manner. The corks are now withdrawn and one end of the cell is sealed and another platinum wire E_2 fused into it. With a little practice the cell can be constructed in less time than it takes to make an H-form of cell.

The cell now appears as in Fig. 2. If it is to be used in a water thermostat, it may be placed in a test-tube containing an oil such as kerosene, to prevent short-circuiting; or the wire E_1 may be replaced by another sealed into a small tube which may pass through a cork above or may be sealed into the cell 5 or 6 cm. above the bulb F and pass down inside to a point just above F.

The cell is filled as follows:

Put mercury in the bottom of the tube by means of a small pipette or funnel made by drawing out a test-tube. Above this place the mercurous sulphate paste and cadmium sulphate crystals by means of a small tube. Then by means of a pipette put into the cell sufficient saturated cadmium sulphate solution to fill the bulb F. Air will thus be entrapped below F, and to remove it apply suction at the end of the cell. On removing the suction the solution will rush down to fill the space below the bulb. Now press some asbestos or glass-wool down through the inside tube to fill the bulb F, packing it in fairly tightly, yet not so compactly as to make the internal resistance of the cell too great. Then put enough cadmium amalgam in the space above F to cover the platinum wire E_1 completely. Above this place cadmium sulphate crystals and add enough saturated cadmium sulphate solution to fill the cell about a centimeter above the end of the inside tube. Several centimeters above this, seal up the tube or insert a cork and the cell is completed as represented in Fig. 3. The Clark cell may of course be set up in the same way.

It is impossible to mix the contents of the anode and cathode compartments. If the cell is turned over the mercury runs down and is caught below the bulb, and when the tube is placed erect again the mercury returns to its original position. The amalgam, if

it moves at all, will behave in a similar manner. If any mercury or amalgam or mercurous sulphate falls into either end of the inside tube, the asbestos in the bulb will prevent it from going into the other compartment.

The H-form of cell is made transportable by employing a similar "double-trap" in the cross-tube connecting the two legs, as shown in Fig. 4. In this case the asbestos should be put into the bulb before the cross-tube is sealed to the legs.

Some cells like the above were made during the past year in the laboratory of physical chemistry, Princeton University, while working under the direction of Dr. Hulett on the subject of standard cells, in fact this cell is a modification of a form suggested by Dr. Hulett. Transportation and rough treatment have not caused the contents of the two compartments of these cells to mix in the slightest degree.

Dominion Astronomical Observatory,
Ottawa, October, 1907.

A DEVICE FOR PREVENTING BUMPING IN THE MERCURY AIR-PUMP.

By Ralph E. DeLury.

IN the use of the mercury air-pump one experiences the disagreeable "bumping" of the mercury, which sometimes results in the breaking of the pump. This may be avoided by using the device described below.

In Fig. 1 the ordinary form of air-pump is represented. The

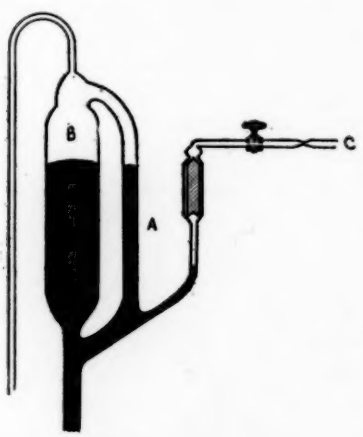


Fig. 1.

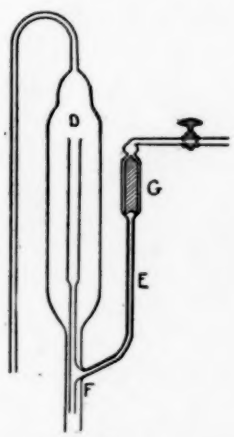


Fig. 2.

"bumping" is caused by the impact of the mercury which is shot up the side tube *A* with a velocity depending on the difference of pressure in the bulb *B* and the apparatus to be exhausted *C*. In a measure this may be stopped by not exhausting *B* so completely that there is a great difference of pressure in *B* and *C*. However the trouble is completely removed by replacing the side tube *A* by a tube inside the bulb, such as *D*, Fig. 2. The tube *E* is a thick-walled tube of about 2 mm. bore. It is sealed into the side of the vertical tube at *F* and inside *F* it makes a T-seal with *D*. The

tube *D* is open at both ends. The lower part of *D* should be about 4 mm. in diameter, and the upper part about twice this bore.

If now the mercury be caused to rise it will flow up through *D* and the bulb around it, and up into tube *E* until it closes the valve *G*. The air is forced out of the bulb and when the mercury flows back the pressure in *E* will cause the air to enter tube *D* before the mercury is all out of it. The mercury in *D* will thus be forced upwards as the air from *E* expands into the vacuum above, but since *D* is larger than *E* the mercury sprays very gently out of the end of *D*. Even if the mercury were shot up swiftly through *D* it would strike the solid curved top of the bulb without danger of breaking it or without causing the pump to vibrate transversely as is the case in the ordinary form.

A pump of this construction, used along with a water suction for lifting and lowering the mercury, has proved to be very satisfactory.

DOMINION ASTRONOMICAL OBSERVATORY,
OTTAWA, October, 1907.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-EIGHTH MEETING.

THE Fall meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, October 19, 1907, President Edward L. Nichols presiding.

The following papers were presented:

1. Results of Careful Weighings of a Magnet in Various Magnetic Fields. L. A. BAUER.

2. On the Emissivity of Molten Iron and Copper. C. B. THWING.

3. The Selective Reflection characteristic of Salts of Carbonic and other Oxygen Acids. LEIGHTON B. MORSE.

4. The Variation of the Light Sensitiveness of the Selenium Cell with Pressure. F. C. BROWN and JOEL STEBBINS.

5. The Recovery of Selenium Cells after Exposure to Light. ERNEST MERRITT.

6. Wave-length — Luminosity Curves for Normal and Color-blind Eyes. F. L. TUFTS.

7. The Behavior of Selenium under the Action of Radium Rays, and some Recovery Curves for the Same. F. C. BROWN.

8. An Investigation of the Electric Displacement and Intensities Produced in Insulators by their Motion in a Magnetic Field, and its Bearing on the Question of the Relative Motion of Æther and Matter. (Read by title.) S. J. BARNETT.

It was announced that the usual Thanksgiving meeting in Chicago would be omitted, and that the Physical Society would meet in Chicago during Convocation Week in connection with the meeting of the American Association for the Advancement of Science.

Adjourned.

ERNEST MERRITT,
Secretary.

RESULTS OF CAREFUL WEIGHINGS OF A MAGNET IN VARIOUS MAGNETIC FIELDS.[1]

BY L. A. BAUER.

A DISCUSSION of the results obtained by the magnetic survey yacht "Galilee" in the Pacific Ocean led the author to the tentative assumption, as announced at the meeting of the society last spring, that the earth's action on a magnet might not necessarily be everywhere that of a couple. Owing to the nonfulfillment, for one cause or another, of the conditions necessary to produce an exact couple there would be in addition a resultant force of translation. The cause may be a purely artificial one, due to some instrumental defect, *e. g.*, magnetic impurities in the metal used, or a natural one because of lack of uniformity in the magnetic field at the place of observation.

This hypothesis has been subjected by the writer during the past summer to a series of preliminary tests, involving careful weighings of a magnet, using a non-magnetic Becker analytical balance, embracing the region of the earth from Washington, D. C., to Sitka, Alaska.

The magnet was weighed in two horizontal positions (north end towards magnetic north and next reversed so that north end was towards magnetic south) and also in two vertical positions (north end up and north end down). The weighings were made at Sitka (Alaska), Victoria (British Columbia), Baldwin (Kansas), and Washington, D. C. At these places the earth's magnetic field is approximately uniform, *i. e.*, no marked local disturbances are known to exist.

The magnet was invariably weighed in both scale pans and the weighings in general were extended over two days at each station. In general the result for magnet, north end south, was greater than for north end north, the average difference being nearly $\frac{1}{1000000}$ part of the weight of the magnet (about 33.6 grams). The differences in the weighings for the two vertical positions ($U - D$) were sometimes positive and sometimes negative, the average, regardless of sign, being of about the same order of magnitude as for the horizontal positions.

Weighings were also carried out in the intensely locally disturbed area at Treadwell Point, Douglas Is. (Alaska). Here the average difference for four points of observation was 0.07 mmg. (about $\frac{1}{500000}$ part) in the case of the two horizontal positions of magnet (weight for north end south being again greater) and for the two vertical positions, 0.25 mmg. or nearly $\frac{1}{100000}$ part (weight north end down being the greater). The

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 19, 1907.

differences are thus more pronounced — as was to be expected — than for the comparatively undisturbed fields.

Upon return to Washington, the investigation was amplified so as to embrace another magnet of different style, make and magnetic moment, and the weighings made for eight equidistant orientations of magnet (north end towards magnetic north, NE., E., etc.). Besides this, the balance itself was "swung" in order that the beam would not always be directed in the same way for the same orientation of magnet so as to exclude in every way possible any effect that might be attributed to magnetic impurities remaining in the balance, which the special tests failed to disclose. It was found that the orientation of *balance* had no appreciable effect upon the results obtained.

However, a systematic curve of differences or residuals from the mean weight, for the eight orientations of *magnet*, resulted — somewhat similar to the deviation curves which represent the effect on the compass of the iron on board a vessel. Two waves of about the same amplitude were clearly discernible — a semicircular one and a quadrantal one — the latter apparently associated with the inductive effect of the earth on the magnet in its various positions. On account of the presence of the quadrantal term, reversal of magnet does not eliminate the effect on the weight due to the outstanding residual magnetic force of translation. Hence the mean result of weighings of a magnet in two positions 180° apart will not necessarily give the true weight, or say the weight which the same substance would have if demagnetized. This was proved also by repeated magnetizations and demagnetizations of two different magnets. To get the true weight of a magnet within the accuracy attainable with the balance used, the weighings of the substance when magnetized would have to be made for *at least* eight equidistant positions.

The observations were repeated on three days, October 10, 11 and 12, at the Coast and Geodetic Survey Magnetic Observatory at Cheltenham, Md., and practically the same results obtained as before.

For the two stations, Washington and Cheltenham, the range in the results for the various orientations of magnet was about 0.05 mmg. ($\frac{1}{2000000}$ part of weight of magnet).

The investigation is being continued.

THE SELECTIVE REFLECTION CHARACTERISTIC OF SALTS OF CARBONIC AND OTHER OXYGEN ACIDS.[1]

BY LEIGHTON B. MORSE.

I. *The Selective Reflection of Carbonates as a Function of the Atomic Weight of the Base.*

POLISHED plane surfaces of (Mg, Ca, Fe, Mn, Zn, Sr, Ba and Pb) CO_3 were prepared and the ratio of the reflected to the incident radiation was measured at short wave-length intervals between 4 μ and 15 μ. The following are the principal conclusions reached:

1. The reflection curves for all the carbonates examined show between 4 μ and 15 μ three and only three bands of abnormal reflection. Abnormal reflection interpreted means a free resonance period of the molecule.

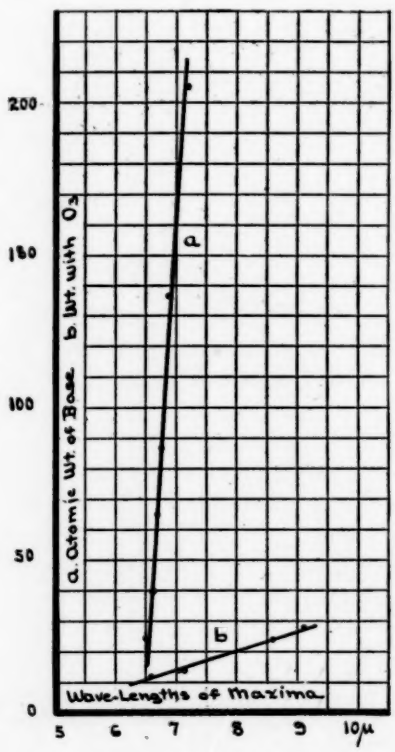


Fig. 1.

2. The bands fall into three separate and definite spectral regions, which are distinct from the regions where the salts of other acids, so far as known, show reflection maxima.

3. With few exceptions, an increase in the atomic weight of the base causes a shift of all three reflection maxima toward long waves of an amount roughly proportional to the change in atomic weight of the base. This is shown for the first reflection band by curve *a*, Fig. 1, in which the atomic weights of the bases are plotted as ordinates and the wave-lengths of the first reflection maxima as abscissæ.

II. *The Rôle Played by Oxygen in the Selective Reflection of Carbonates, Nitrates, Sulphates and Silicates.*

Combining with the data on carbonates the scattered observations of other observers on nitrates, sulphates and silicates, the tentative hypothesis has been made that the

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 19, 1907.

oxygen atom is the one chiefly responsible for the marked reflection observed.

The wave-lengths of the first reflection bands in $CaCO_3$, KNO_3,[1] $CaSO_4$ and $MgSiO_3$[2] are plotted as abscissæ, curve *b*, Fig. 1, and as ordinates, the weights of the acid-forming elements combined with O_3, (C = 12; N = 14; $\frac{3}{4}$S = 24, and Si = 28).

The lines drawn show clearly that a small increase in the weight of the acid-forming element produces a much greater displacement of the reflection band than does the same increase in the weight of the base; and this is in full agreement with the chemists' view of the relative strength of the bond existing between the *acid-forming element* and oxygen and that between the *base* and oxygen.

The results suggests a new and far-reaching method by which it may sometimes be possible to express the dynamical relations existing between the separate atoms of a molecule, and thus the present conception of chemical bonds and linkages be given a broader significance.

The paper appears in full in the *Astrophysical Journal* for November, 1907.

The Variation of the Light Sensitiveness of the Selenium Cell with Pressure.[3]

By F. C. Brown and Joel Stebbins.

THIS investigation is a continuation of the work reported to the American Physical Society at its February meeting in 1905, when it was shown for pressures from 0 to 600 atmospheres that the change of resistance of the selenium cell was approximately a linear function of the pressure.

It deals chiefly with the results of observations of the light effect at different pressures and states the results of a comparison of the light effect at different pressures with the light effect at different temperatures.

The following is a summary of the observations taken with a Giltay cell of which .3 sq. cm. of the surface was illuminated by a one c.p. incandescent light at 30 cm. distance. Each series is obtained from the average of fifteen exposures.

From these and other data the following conclusions were made:

1. The pressure effect is a genuine effect in the selenium itself and not a change in the contact resistance between the electrodes and the selenium or between parts of the selenium itself.

[1] Two values are plotted for KNO_3 corresponding to the results obtained by two independent observers, Pfund and Coblentz.

[2] If a correction be applied to correct for Mg being lighter than Ca this would bring the $MgSiO_3$ point even nearer the line drawn.

[3] Abstract of paper read before the American Physical Society, October 19, 1907.

2. The light effect decreases with pressure when expressed in ohms or in percentage.

Series.		I.	II.	III.	IV.
Resistance of cell in ohms	pressure on	2,607,000	2,270,000	2,133,000	1,915,000
	pressure off	2,850,000	2,878,000	2,435,000	2,530,000
Mean pressure in pounds		730	2,075	520	1,930
Change in resistance due to light	pressure on	185,000	131,000	149,000	164,000
	pressure off	220,000	200,000	178,000	245,000
Percentage change of resistance due to light	pressure on	7.11	5.77	6.99	8.59
	pressure off	7.70	6.92	7.32	9.70
Change of light effect due to pressure		0.59	1.15	0.33	1.11
Change of light effect per lb. pressure		.00083	.00056	.00065	.00058

3. The percentage decrease of resistance due to light is a function of the initial resistance, whether this initial resistance be conditioned by pressure or temperature.

THE RECOVERY OF SELENIUM CELLS AFTER EXPOSURE TO LIGHT.[1]

BY ERNEST MERRITT.

IT has long been known that the increase in the conductivity of selenium that results from illumination is not an instantaneous effect. It is necessary to wait a considerable time after the exposure to light has begun before the final steady value of the resistance is reached. The recovery of selenium after illumination is even slower. In some cases the cell must be kept in the dark for several hours before the resistance comes back to its original value. While several observers have recorded observations which illustrate this gradual recovery, and which in some instances make it possible to plot a curve showing the relation between resistance and time, the subject does not appear to have attracted very great attention.

The writer has recently made observations on the recovery of selenium cells as influenced by the duration and intensity of the previous excitation, and finds a remarkable resemblance between the behavior of selenium, as indicated by the change in its conductivity, and the behavior of a phosphorescent substance, as indicated by the intensity of its phosphorescence. It was in fact the expectation that such a resemblance would obtain that led to these observations being made.

The cell used had a resistance in the dark of about 50,000 ohms. It was placed in a circuit containing a dead beat galvanometer and an E.M.F. of

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 19, 1907.

about 1 volt, and was excited by an acetylene flame at a distance of about 40 cm. The curves of Fig. 1 correspond to excitations of 10 seconds, 30 seconds and 300 seconds respectively. The method of plotting the curves is to take the difference between the observed conductivity C and the normal conductivity C_0 (measured in the dark), and to plot as ordinates the values of $(C - C_0)^{-\frac{1}{2}}$. This method of plotting was suggested by the results obtained by Nichols and Merritt for the decay of phosphor-

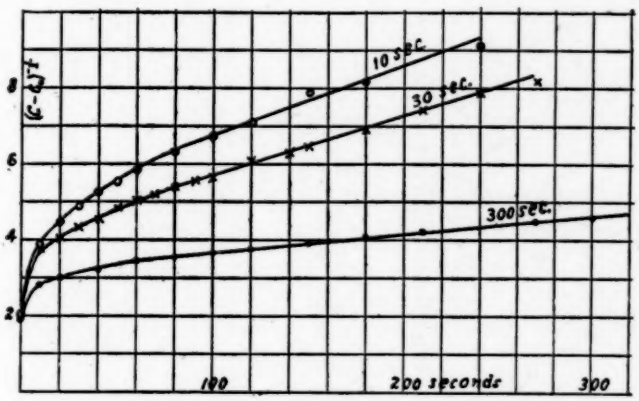


Fig. 1.

escence in Sidot blende,[1] where a linear relation between $I^{-\frac{1}{2}}$ and t was found to hold after the first 40 seconds. The effect produced by light in Sidot blende is indicated by the intensity I of phosphorescence, while in selenium the effect of light is indicated by the *increase* in conductivity $C - C_0$. In order to facilitate a comparison of the behavior of selenium and Sidot blende a group of decay curves for the latter substance is shown in Fig. 2, this figure being reproduced from the article just referred to. In the curves of Fig. 2 the excitation was varied from 1.2 seconds in curve A to 900 seconds in curve F.

The resemblance between the two groups of curves is so striking as to suggest some real similarity between the two processes. In each case the curves start out concave toward the axis of t, but soon change into lines that are so nearly straight that the deviation is less than the experimental errors. The effect of increasing the duration of excitation is in both cases to prolong the time required for recovery, *i. e.*, to make the straight part of the curve more nearly horizontal.

In the case of Sidot blende, Nichols and Merritt have found that the relation between $I^{-\frac{1}{2}}$ and t is also linear during the first seven seconds of

[1] PHYSICAL REVIEW, Vol. XXIII., p. 37, 1906.

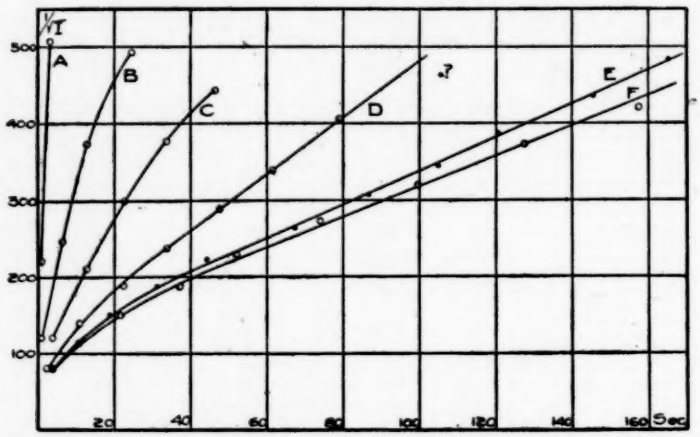


Fig. 2. Effect of duration of excitation upon the phosphorescence of Sidot blende. The times of excitation were as follows :

Curve *A*, 1.2 sec.
" *B*, 5.4 sec.
" *C*, 12.0 sec.
Curve *D*, 37 sec.
" *E*, 60 sec.
" *F*, 15 min.

decay,[1] so that the complete curve seems to consist of two straight portions connected by a region of rather sharp curvature. By the method thus far used with selenium I have not been able to make observations within the first 10 seconds. I find, however, that the recovery of selenium

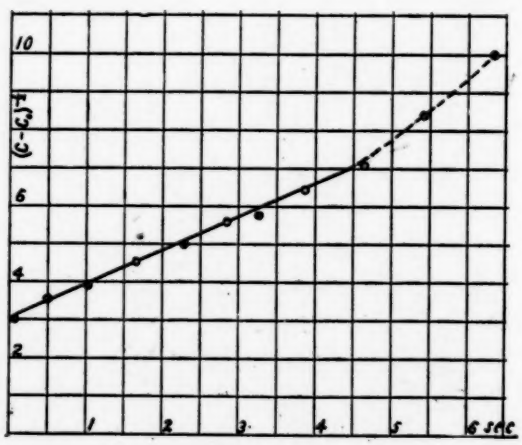


Fig. 3.

during the first few seconds after the end of excitation has been studied by Majorana[2] whose results, plotted in the manner explained above, are

[1] PHYSICAL REVIEW, Vol. XXII., p. 279, 1906.
[2] Rendiconti dei Lincei (5), 3, p. 183, 1894.

shown in Fig. 3. It will be noticed that the relation between $(C - C_0)^{-\frac{1}{2}}$ and t is linear for the first 5 seconds.[1] The behavior of selenium thus seems to be similar to that of Sidot blende in the earlier stages of recovery as well as later.

Another resemblance between the two phenomena is met with when we consider the effect of varying the intensity of excitation. In the case of Sidot blende a series of decay curves taken with constant time of excitation but increasing intensity is found to be somewhat similar to a series taken with constant intensity and increasing duration.[2] I have found that the same is true with selenium.

It seems not unlikely that the sharp curvature of the curves of Figs. 1 and 2 in the early stages of decay is due to the fact that the exciting rays penetrate only a short distance below the surface. The surface layer is in consequence excited far more strongly than the interior and decays with corresponding rapidity. After a short time the conditions will be more nearly uniform throughout and the decay will be more gradual. If experiments could be made with a sufficiently thin layer it seems not unlikely that the curves would be straight throughout their whole course.

If the increased conductivity of selenium produced by light is due to temporary dissociation, as has been suggested by Bidwell, it is of interest to note that the linear relation between $(C - C_0)^{-\frac{1}{2}}$ and t corresponds to a substance of the type $CuCl_2$.

The Effect of Radium on the Resistance of the Selenium Cell.[3]

By F. C. Brown and Joel Stebbins.

THE work in this paper was with a Ruhmer cell when exposed to radium of from 2 to 3 million activity. Two series of curves were shown showing the decrease of resistance with time of exposure, when the distance of the radium varied from .1 inch 4.1 inches. Another series of curves were shown showing the decrease of resistance with time of exposure when different thicknesses of mica were interposed between the radium and the selenium. And still another series of curves were shown showing the recovery of resistance with time. The amount of decrease of resistance varied from 30 to 0 per cent.

[1] The deviation of the last two points from the straight line does not possess great significance, since when $C - C_0$ is small the value of the corresponding ordinate will be greatly influenced by small errors in either C or C_0.

[2] Nichols & Merritt, Physical Review, Vol. XXII., p. 37, 1906.

[3] Abstract of paper read before the American Physical Society, October 19, 1907.

From these curves it was shown that the decrease of resistance was due chiefly to the action of the β-rays. The variation of resistance change with distance was also deduced.

The rate of recovery from radium exposure was found to be about five times less than for light exposures of short duration.

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